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EQUILIBRIUM VOLATILITY OF MOTOR FUELS FROM THE STANDPOINT OF THEIR USE IN INTERNAL COMBUSTION ENGINES

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ABSTRACT

One of the larger problems in connection with the relation between fuel characteristics and engine performance is concerned with fuel volatility. For many years, the National Bureau of Standards conducted an investigation of fuel volatility, in cooperation with the automotive and petroleum industries, and the present paper covers the experimental data obtained and the conclusions reached in this investigation. An apparatus and method are described for the measurement of the equilibrium volatility of motor fuels, and experimental data are presented on 38 gasolines and blends covering a wide range of volatility. A correlation is shown to exist betwen equilibrium volatility data and distillation data obtained by the standard A.S.T.M. method. By use of the equations deduced, it is possible to obtain from distillation data all of the equilibrium volatility data of interest in connection with engine performance.

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I. THE PRACTICAL PROBLEM OF MOTOR FUEL VOLATILITY

The advent of the automobile and the phenomenal growth of the automotive industry changed the status of gasoline from a byproduct of little commercial value to the major product of the petroleum industry. The new market for gasoline, thus created, stimulated the rapid expansion of the petroleum industry, resulting in extensive development of the national oil resources and improvements in refinery technology. Thus the last two decades have seen the rise concurrently of two of the major industries of the country, each dependent upon the other, but until recently neither industry has been in possession of requisite information for satisfying the requirements of the other. The immediate problem confronting the industries, therefore, was to secure adequate knowledge of the best engine design for operation with existing fuels and of the most satisfactory fuel for use with existing engines. The ideal solution, hoped for, was the acquisition of sufficient information to permit that mutual adaptation of engine design and fuel characteristics which would result in maximum economies for both industries.

1. THE AUTOMOTIVE INDUSTRY PROBLEM

One of the major problems of the automotive industry has always been to design engines which would give the desired performance with current fuels. The engine should start readily even in cold weather and should keep on running without too many interruptions. The induction system should take care of adequate distribution of the charge to the various cylinders and should permit the automobile to accelerate rapidly. Heating of the intake manifold should be sufficient to vaporize most of the fuel in order to minimize dilution of the crankcase oil. The fuel feed system should be constructed so that the fuel is fed in the desired amounts to the intake manifold without serious interruption of flow due to vapor lock.

In order to design equipment which will satisfy these requirements, the automotive engineer must know how the fuel behaves in the engine and what characteristics of the fuel determine this behavior. He is also interested in specifying the type of fuel for which his engine is designed and on which it will operate satisfactorily, and in having information on the ability of the oil refiner to supply an adequate amount of such fuel at a reasonable price.

2. THE PETROLEUM INDUSTRY PROBLEM

The petroleum technologist also should know how the fuel behaves in the engine in order that he may intelligently produce the most satisfactory fuel for use in engines of current design. He should know, still further, the characteristics of fuels which determine their performance in the engine and he should have adequate routine tests for the evaluation of these characteristics. Then with knowledge of what gasoline for use in existing types of engines ought to be and with sufficient information to enable him to determine when he has such a fuel, the oil refiner is in a position to develop his refinery technique to the point where he can produce a consistently satisfactory fuel from the minimum amount of crude oil.

3. THE COOPERATIVE FUEL RESEARCH AND THE PRACTICAL VOLATILITY PROBLEM

In 1922 the automotive and petroleum industries combined in financing cooperative fuel research at the National Bureau of Standards on important problems of common interest under the supervision of a steering committee composed of representatives from the three cooperating groups. This fuel research has had for its one guiding principle the mutual adaptation of the fuel to the engine and the engine to the fuel. Insofar as has been feasible, work on the various projects undertaken has been conducted simultaneously from the standpoint of the fuel characteristics and the behavior in the engine.

One of the larger problems investigated was the relation between fuel volatility and engine performance. When a fuel is used in the engine, there are two portions of the fuel system in which volatility is of interest in connection with performance. These may be characterized as the fuel feed system, including all parts up to the carburetor jet, and the induction system, in which the fuel is in contact with air. In the former, volatility is connected with vapor-locking tendency; whereas, in the latter, volatility is linked with starting, acceleration, and crankcase dilution. In both of these cases, the optimum volatility is dependent to a greater or less extent upon the individual characteristics of each engine and equipment and upon the conditions of use.

Accordingly, a practical investigation of fuel volatility from the automotive standpoint should involve (1) an evaluation of those fuel characteristics which affect the various phases of engine performance under conditions of operation, and (2) the development of test methods for the determination of these volatility characteristics.

4. SCOPE OF THE PRESENT PAPER

Those properties of fuels which determine their tendency to cause vapor lock in the fuel feed system will not be considered in the present paper, and reference will be made only to those characteristics which affect vaporization in the presence of air. Because the extent of vaporization in the induction system is specific for each type of equipment, the first step in the study of fuel volatility should yield results of general applicability and independent of the particular conditions existing in any one induction system. Data so obtained for an ideal manifold represent limiting values approximated to varying degrees by different systems, and furnish the fundamental information necessary for an intelligent investigation of volatility under actual operating conditions.

The volatility work has been confined to this first step in the study of vaporization in the presence of air. Until a study of the application of these data to actual manifolds is undertaken, the somewhat plausible assumption is necessary that the order of the volatilities of a series of fuels under equilibrium conditions is unchanged when these fuels are used in any given engine induction system.

II. ANALYSIS OF THE VOLATILITY PROBLEM

1. CHOICE OF VARIABLES

Volatility is a measure of the tendency of a substance to evaporate or to change from liquid to vapor under given conditions. It may be expressed in terms of the pressure exerted by the vapor under each set of specified conditions. One of the conditions which must be specified is the temperature, for the vapor pressures of all substances increase with temperature. Another condition which must be specified in the case of composite liquids, like gasolines, is the composition of the liquid at the time when the vapor pressure is measured.

With a one-component substance, such as water, the vapor pressure at a given temperature remains constant regardless of how much water evaporates. When more than one component is present, this is no longer true, since the more volatile constituents evaporate more readily, leaving the residual liquid less and less volatile as evaporation progresses. With a substance like gasoline, containing possibly several hundred hydrocarbons, the change in vapor pressure as evaporation progresses is very marked, since the less volatile components have a lower vapor pressure and since the proportion of these less volatile components in the residual liquid becomes greater as more of the liquid evaporates. This means that not only must the temperature be specified in the case of gasolines, but the composition of the liquid must also be specified.

Specification of the chemical composition of a gasoline is in general almost impossible at present, due to the indeterminate number of hydrocarbons present in unknown amounts. While it may be feasible to separate a simple natural gasoline into various groups by fractional distillation and thereby arrive at its approximate composition, even this method is not practicable for the average refinery product. With any specific gasoline, it is not necessary to know the chemical composition for, at any given temperature, the vapor pressure is defined at each point when the percentage evaporated is specified. If percentage evaporated is thus used to indicate composition, it is necessary to have some means of identifying each gasoline. Such identification is furnished by the distillation curve.

When a gasoline is delivered by the carburetor to the induction system, it is mixed with air in the requisite proportions. The mixture supplied is expressed in terms of the weight of air per unit weight of gasoline, which is commonly called the air-fuel ratio. The resultant mixture formed when part or all of the liquid evaporates is also expressed in terms of the weight of air per unit weight of gasoline vapor. Hence although the pressure of the vapor is the fundamental variable involved at any temperature and percentage evaporated, a more convenient variable, related to pressure, is the resultant mixture ratio of air and gasoline vapor formed at this temperature and percentage evaporated. In this case, it is necessary to specify the total pressure of the mixture and this has been fixed at one atmosphere, which is equal to 760 mm of mercury under standard conditions or 14.7 lb/in.^{2}

By the use of these variables, volatility is specified in terms of the practical units used by the industry. Volatility is therefore defined for the present purpose in terms of the temperature at which a given air-vapor mixture is formed under equilibrium conditions at a pressure of one atmosphere, when a given percentage is evaporated. According to this definition, one gasoline is more volatile than another for any given percentage evaporated if it forms the given air-vapor mixture at a lower temperature.

2. RANGES OVER WHICH VARIABLES REQUIRE INVESTIGATION

In order that an engine may start and run without interruption, it is necessary that an explosive mixture of air and fuel vapor be supplied to the cylinders at all times during the period of operation. The practical range of explosive air-vapor mixtures is from 4:1 to 20:1 by weight. Accordingly, at each percentage evaporated, this limits the range of resultant mixtures which require investigation.

When an engine is being started in cold weather, a very rich mixture must be supplied by the carburetor since the percentage of the fuel which evaporates under these conditions is small and enough must be evaporated to produce an explosive mixture. As the engine warms up, a larger percentage evaporates and accordingly a leaner mixture can be supplied by the carburetor. Finally, when the engine is being run under steady operating conditions, the resultant air-vapor mixture is not much leaner than the supplied mixture because most of the fuel evaporates.

Hence, since different percentages of the fuel evaporate under different operating conditions, the mixture supplied by the carburetor must be adjusted so that the resultant mixture is always in the explosive range from 4:1 to 20:1. The limits of the percentage of fuel evaporated under operating conditions range from very small percentages to complete evaporation, so that the study of fuel volatility should include measurements at values of the percentage evaporated covering the range from 0 to 100 percent.

3. SUBDIVISION OF THE VOLATILITY INVESTIGATION

A diagrammatic example for one gasoline of the volatility field of interest in connection with automotive engines is shown in figure 1. The hatched area, labeled "Automotive Volatility Field", covers a range for this gasoline of air-vapor mixtures bounded by the 4:1 to 20:1 air-vapor lines and of percentages evaporated from 0 to 100 percent. For gasolines with different evaporation curves, similar volatility fields will be obtained but displaced to an extent dependent upon the differences in distillation characteristics. Each point in the field represents the resultant air-vapor mixture formed under equilibrium conditions at that temperature and at the given percentage evaporated for a total pressure of one atmosphere. Each air-vapor line is a volatility curve and is called the resultant equilibrium air-evaporation curve. It represents an equilibrium distillation or evaporation in the presence of air under such conditions that all of the vapor formed is confined in the presence of the residual liquid under a total pressure of one atmosphere. The upper curve in the figure is the A.S.T.M. evaporation curve of the fuel (see definition,

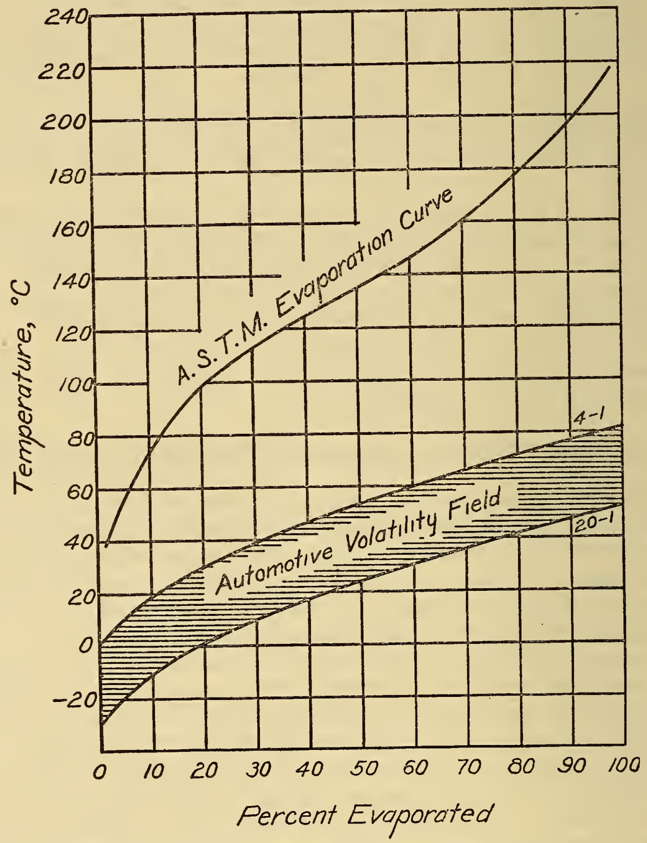

Figure 1.—*Illustration of the volatility field of interest in connection with engine performance as compared with the A.S.T.M. evaporation curve.*

sec. III). It represents a nonequilibrium distillation or evaporation at atmospheric pressure under such conditions that the vapor formed is removed in a specified manner from contact with the residual liquid under a total pressure of one atmosphere. The A.S.T.M. evaporation curve is used to identify the gasoline.

The vertical line of 100 percent evaporated represents the temperatures corresponding to complete equilibrium vaporization of the various supplied air-fuel mixtures. This line also represents the temperatures at which liquid would just separate out under equilibrium conditions on cooling the superheated resultant air-vapor mixtures. Hence temperatures along this line are called dew points, and the chemical composition of the gasoline vapor is the same at every temperature, being identical with the composition of the unvaporized liquid gasoline. The composition of the liquid which separates out will, however, vary with temperature.

The vertical line of 0 percent evaporated represents the temperatures at which a bubble would form under equilibrium conditions in the liquid gasoline saturated with air under a total pressure of one atmosphere. Hence temperatures along this line are called bubble points. At different temperatures, the ratio of air to fuel vapor in the bubble will be different and the chemical composition of the fuel vapor will vary. The composition of the liquid gasoline will, however, be the same at all temperatures.

At every intermediate percentage between 0 and 100 percent, where both liquid and vapor are present simultaneously in more than infinitesimal amounts, the chemical composition of each is different at every temperature and neither liquid nor vapor has the same composition as the original gasoline. Data at intermediate percentages are called partial volatility data.

III. DEFINITIONS OF TECHNICAL TERMS USED

A summary of definitions of a number of the technical terms used in this paper is given below:

Volatility is the tendency of a substance to evaporate or to change from liquid to vapor under given conditions. For the present purpose, it is expressed quantitatively in terms of the temperature at which a given resultant air-vapor mixture will be formed under equilibrium conditions at a pressure of one atmosphere, when a given percentage is evaporated.

Supplied air-fuel mixture (supplied mixture or air-fuel mixture) is the ratio by weight of the amount of air to that of liquid fuel supplied. As used in this paper, the total pressure is one atmosphere, unless otherwise stated.

Resultant air-vapor mixture (resultant mixture or air-vapor mixture) is the ratio by weight of the amount of air to that of fuel vapor formed from the supplied mixture. The total pressure of air and fuel vapor is taken to be one atmosphere, unless otherwise stated.

Equilibrium vaporization is the vaporization under such conditions that all of the vapor formed is confined in the presence of the residual liquid for a period of time sufficiently long so that any increase in the time would not increase the amount which evaporates under otherwise unchanged conditions.

Equilibrium air-evaporation is the vaporization under equilibrium conditions in the presence of air. The total pressure is one atmosphere, unless otherwise stated.

Equilibrium air-evaporation curves are the curves obtained by plotting temperature against percentage evaporated for a constant resultant air-vapor mixture.

A.S.T.M. evaporation curves are curves obtained by plotting the temperatures recorded in the standard A.S.T.M. distillation test against the percentage evaporated, which is obtained by adding the distillation loss to the percentage distilled at each point.

Percentage evaporated is the amount of liquid which evaporates under given conditions, expressed in percent. When used in this paper in connection with the volatility data, it is expressed in weight percent. When used in connection with A.S.T.M. evaporation data, it is expressed in volume percent.

Dew point is the temperature corresponding to initial liquid formation under equilibrium conditions on cooling a given superheated resultant air-vapor mixture. It is also the temperature corresponding to complete equilibrium vaporization of a given supplied air-fuel mixture. It is the point at which a given equilibrium air-evaporation curve intersects the line of 100 percent evaporated. Unless otherwise stated, it refers to a total pressure of one atmosphere.

Bubble point is the temperature at which a bubble, composed of a given air-vapor mixture, is in equilibrium with the unvaporized liquid gasoline, saturated with air under a total pressure of one atmosphere. It is the point at which a given equilibrium air-evaporation curve intersects the line of 0 percent evaporated. Unless otherwise stated, it refers to a total pressure of one atmosphere.

Partial volatility data are data applying to percentages evaporated intermediate between 0 and 100 percent.

IV. A.S.T.M. EVAPORATION DATA ON FUELS USED IN VOLATILITY WORK

A.S.T.M. evaporation data were obtained on all of the fuels used in the volatility work. These data were primarily intended for identification but after volatility results on a number of fuels had been obtained, a relation was found to exist between the A.S.T.M. evaporation and the volatility data. Accordingly, extreme care was taken in making the A.S.T.M. distillations.

For all the gasolines, the American Society for Testing Materials Standard Method D86–27 was employed [1] and all detailed directions were carefully followed. In two respects, temperature was controlled more closely than required by the standard A.S.T.M. method. By using a mixture of finely shaved ice and water, the temperature of the condenser was maintained as closely as possible at 0 C, rather than at temperatures within the permissible range of 0 to 4.5 C. Further, in the initial measurement of the sample, the actual temperature of the gasoline, within the permissible range of 12.8 to 18.3 C, was noted and throughout the entire distillation the temperature of the liquid bath surrounding the receiver was kept at this value within 1° C. In this manner, better reproducibility was obtained and greater precision in the determination of distillation loss was possible.

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[1] A.S.T.M. Standards, 1927, p. 378, published by the American Society for Testing Materials, Philadelphia, Pa. This method was revised to a minor extent in 1930, under the designation D86–30, but this revision does not affect the conclusions reached in the present paper.

The magnitude of the possible error in distillation loss by taking advantage of the extreme temperature range, permitted by the A.S.T.M. method, can be shown by an example. Suppose a gasoline of specific gravity 0.720 at 60 F/60 F has 2.0 percent distillation loss when measured and collected at 15.6 C. If the sample is measured at 18.3 C, and is collected at 12.8 C, the apparent loss will be 2.6 percent. If, however, it is measured at 12.8 C and collected at 18.3 C, the apparent loss will be 1.4 percent. In either of these cases, there will be an error of 0.6 percent, and there may be a difference of 1.2 percent in duplicate determinations. While the errors may compensate in some cases, the example indicates the possible deviations by the A.S.T.M. method. A control of the temperature so that the sample is measured and collected at temperatures differing by not more than 1° C, reduces the error from this source to 0.1 percent. A more satisfactory procedure would be to measure and collect the sample at 0 C.

Thermometer readings were taken when the first drop fell from the end of the condenser; at every 5 percent recovered throughout the distillation; and when the thermometer reading reached its maximum value. With every gasoline, an A.S.T.M. evaporation curve was obtained by plotting the distillation temperatures against the corresponding percentages evaporated. The percentage evaporated at any point is equal to the percentage recovered plus the distillation loss up to that point. Since the vapor pressure drops very rapidly as the distillation progresses, most of the loss should occur towards the beginning of the distillation. It was therefore assumed that, within experimental error, all of the loss occurred before 10 percent of the sample had been recovered in the receiver, and accordingly the percentage evaporated at every point was considered to be equal to the percentage recovered plus the total distillation loss. Since temperatures below 10 percent evaporated were not used in the correlation with the volatility data, the error introduced in this procedure of correcting for distillation loss should be negligible.

The evaporation curve is simply the ordinary distillation curve displaced to the right by an amount equal to the distillation loss. If the loss is 2 percent and the thermometer reading at 10 percent recovered is 60 C, then in plotting the curve, a mark is made at 12 percent evaporated and 60 C. From the smooth curve through the plotted points for each gasoline, the temperatures were read at every 10 percent evaporated from 10 to 90 percent. These values were then used for the correlation with the volatility data.

Plotting the A.S.T.M. data as evaporation curves places all gasolines on a comparable basis, which is not true of the distillation curves. Further, the method used in obtaining the equilibrium volatility curves precludes any loss, so that the comparison with the A.S.T.M. curves is more logical when the A.S.T.M. data are corrected for loss in the manner indicated.

A description of the 38 fuels used in the volatility experiments is given in table 1. The gasolines contributed by the various oil companies were experimental samples, in many cases prepared specially for the cooperative fuel research work, and they should not be considered as representative of the commercial products sold by these companies. It is believed, however, that the general conclusions drawn from the data on these samples are applicable to commercial gasolines and blends. The list includes 5 aviation gasolines, 5 cracked gasolines, 6 natural gasoline blends, 3 benzol blends, and 3 ethyl ether blends. Identification data on the fuels are given in table 2.

TABLE 1.—*Description of fuels*

Fuel no.	Source	Composition	
1, 2, 3	Atlantic Refining Co	Straight run fuel.	
1A, 2A, 3A, 4A	do	Special blends for starting tests.	
A	National Bureau of Standards	U.S. motor gasoline.	
B	Army Air Corps	Domestic aviation gasoline.	
C	National Bureau of Standards	Equal parts A and B.	
D, E, F	The Texas Co	Special blends for acceleration tests.	
RH	Vacuum Oil Co	Fuel from Grozny crude.	
L	Standard Oil Co. of N.J	Laurel oil.	
6	National Bureau of Standards	U.S. motor gasoline.	
G	do	Fuel 6, 60 percent; motor benzol, 40 percent.	
H	do	Fuel A, 80 percent; benzene, 20 percent.	
I	do	Fuel A, 60 percent; benzene, 40 percent.	
RPC	Universal Oil Products Co.; (cracked by Dubbs process)	Fuels from midcontinent crude.	
J		Smackover crude.	
K		Panhandle crude.	
N		California crude.	
O		Wyoming crude.	
M	National Bureau of Standards	Fuel A, 80 percent; kerosene, 20 percent.	
B3	Army Air Corps	Domestic aviation gasoline.	
101	Naturaline Co. of America	Natural gasoline aviation fuel.	
111	Phillips Petroleum Co	Do.	
121	Virginian Gasoline & Oil Co	Do.	
		Natural gasoline	375 C end-point cracked gasoline
		Percent	*Percent*
S1	Shell Petroleum Corporation	12	88
S2		16	84
S3		22	78
S4		26	74
S5		32	68
S6		52	48
		Ethyl ether	Fuel B3
EB1	National Bureau of Standards	25	75
EB2		50	50
EB3		75	25

TABLE 2.—*Identification data on fuels*

Fuel	A.S.T.M. temperatures at stated percentages evaporated			Loss	Residue	60 F/60 F specific gravity
	10 percent	50 percent	90 percent			
	°C	*°C*	*°C*	*Percent*	*Percent*	
1	114	155	199	1.3	1.7	0.764
2	62	111	195	1.4	1.6	.730
3	91	158	197	1.8	1.2	.755
1A	80	139	195	2.3	1.7	.733
2A	84	139	195	1.5	1.5	.739
3A	93	140	193	1.0	2.0	.738
4A	90	140	186	1.5	1.5	.731
A	75	135	196	1.2	1.3	.768
B	63	101	132	2.0	1.0	.714
C	69	115	174	1.2	1.3	.741
D	89	122	200	.8	1.2	.754
E	84	137	199	.7	1.8	.762
F	72	163	198	1.0	1.0	.766
RH	85	126	168	.5	1.1	.739
RL	72	104	147	.3	1.2	.724
L	117	126	152	.3	1.2	.751
6	92	139	190	1.0	1.0	.768
G	86	107	178	1.0	1.5	.807
H	73	113	186	1.8	1.2	.776
I	76	94	177	1.7	1.3	.805
RPC	66	134	198	1.0	1.5	.747
J	54	135	207	1.6	1.4	.751
K	65	122	176	1.0	1.2	.735
N	96	150	204	.6	1.2	.771
O	82	147	200	.6	1.4	.755
M	89	152	222	.7	1.3	.776
B3	65	105	148	1.6	1.2	.709
101	42	61	106	2.3	1.2	.678
111	53	70	115	1.7	1.3	.684
121	72	79	110	1.1	1.4	.696
S1	64	115	165	.8	1.2	.743
S2	64	114	166	.8	1.2	.735
S3	60	104	161	1.4	1.1	.731
S4	54	103	161	1.3	1.2	.725
S5	52	99	159	1.3	1.2	.719
S6	44	86	154	1.2	1.3	.708
EB1	46	83	128	1.9	1.1	.714
EB2	40	53	124	1.9	1.1	.718
EB3	36	40	112	2.4	.8	.722

V. EQUILIBRIUM AIR-EVAPORATION APPARATUS AND METHOD OF USE

When an engine is being run, a mixture of liquid gasoline and air is supplied by the carburetor to the intake manifold, in which vaporization occurs to an extent dependent upon the design of the manifold, the conditions of operation and the characteristics of the fuel. The most direct method of obtaining volatility data in terms of the variables used in automotive practice is to employ an apparatus in which the process of vaporization is analogous to that occuring in the intake manifold. Such an apparatus was designed by T. S. Sligh [2] at the commencement of this work and was employed throughout essentially in its original form. Known mixtures of air and gasoline are supplied to a vaporization coil maintained at definite temperatures and the amounts of gasoline evaporated are measured. The data thus obtained, when corrected to equilibrium conditions, represent values which would be obtained in an ideal engine manifold. A manifold of this type would be equivalent to a tube, maintained at uniform temperature, of such length that any increase in the length would not increase the amount of fuel vaporized.

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[2] Sligh, SAE Jour., p. 393, April 1926, and p. 151, August 1926.

1. DESCRIPTION OF APPARATUS [3]

Diagrams of the Sligh equilibrium air-evaporation apparatus are shown in figures 2 and 3. In the earlier stages of the work, the temperature range covered did not go below 0 C and the simpler apparatus shown in figure 2 was employed. For extension of the temperature range below 0 C, the more complicated apparatus shown in figure 3 was used. Identical lettering is used for similar parts in the two figures.

The essential part of the equilibrium air-evaporation apparatus is the vaporization coil A, which is a 16-ft length of copper tubing of 7/16 in. outside diameter formed into a helix. Liquid gasoline and preheated air in definite proportions are fed at uniform rates into the top of this coil which is immersed in a well-stirred constant temperature bath. After passage through the coil the unvaporized liquid is separated from the air-vapor mixture in the chamber C and is collected and measured in the burette D, while the vapor passes out through the exhaust pipe E. The flow of gasoline into the vaporization coil is controlled by displacement from the reservoir H by means of the hollow plunger I operated by clockwork. Partial stoppage by the plunger of the overflow tube into the vaporization coil is avoided by providing an offset in the reservoir wall at this point. The plunger is suspended by a fine nichrome wire, 0.008 in. in diameter, which passes through a packing gland L at the top of the reservoir and thence over an idler pulley to connect to a drum K mounted on the spindle of the clock J. The packing gland consists of a thin piece of leather, pierced by a very fine hole for the wire, and mounted between two metal disks which serve to compress the leather and force it tightly

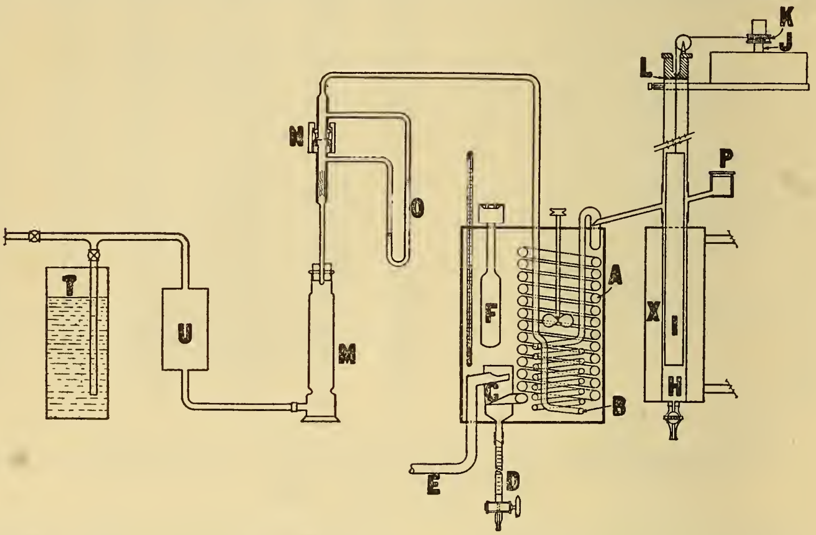

Figure 2.—*Equilibrium air-evaporation apparatus for measurements above 0 C.*

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[3] Preliminary descriptions have been given by Bridgeman and Cragoe, A.P.I. Bull., Jan. 31, 1928, p. 54 and by Bridgeman, SAE Jour., April 1928, p. 437.

around the wire. A recess is provided at the top which was filled with mercury to prevent leakage. The mainspring was removed from the clock, which is driven by the weight of the plunger acting through the drum mounted on the main shaft. The gear train and escapement serve to regulate the motion and to maintain a constant rate of fall of the plunger. To permit rewinding, a ratchet clutch is placed on the top of the clock and engages a gear on the drum. Four drums were used permitting variations in the rate of feed from 1 to 4 ml per minute. The reservoir H was filled through the cup P which was closed with a tight-fitting screw cap during the runs. In the later experiments, a water jacket X was placed around the reservoir in order to control the temperature of the gasoline.

The air used in the experiments was supplied under a slight positive pressure. It was dried by passage through a tower M containing calcium chloride and for the work below 0 C any residual moisture was frozen out by passing the air through a drying tube Q (fig. 3) immersed in a low temperature bath R. This bath was filled either with carbon dioxide slush or liquid air, depending upon the available supply of these refrigerants. The dried air was then heated to about room temperature by means of the electric heater S before passing into the flow meter N. Flat plate orifices were employed to control the air flow, and to reduce turbulence on the high pressure side of the orifice, a number of tubes are placed lengthwise in the air passage as shown in figure 2. The water manometer O indicated the pressure drop across the orifice. Five different orifices were employed, permitting considerable variation in the air flow. For convenience in the interchange of orifices, the flow meter was constructed in two parts joined together by a large threaded union. From the flow meter, the air passed upwards through a small copper coil B for final adjustment of the air temperature before it came in contact with the gasoline.

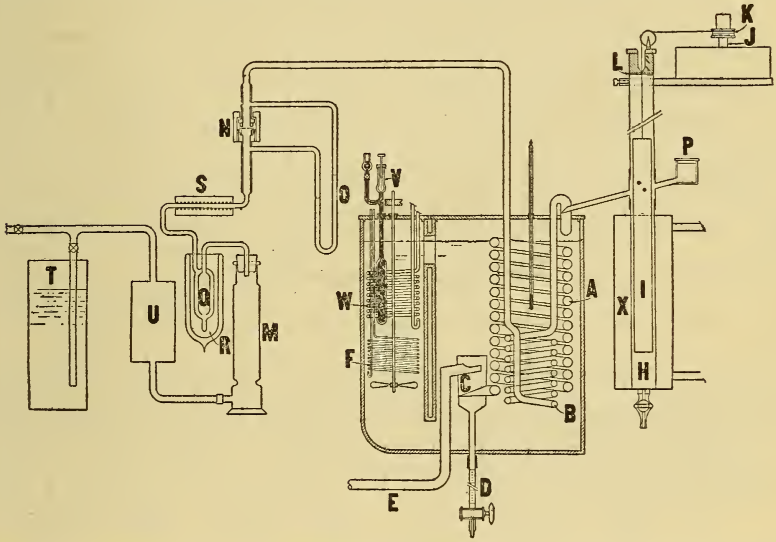

Figure 3.—*Equilibrium air-evaporation apparatus for measurements both above and below 0 C.*

Fluctuations in the air pressure were smoothed out by means of the pressure regulator T and the 5 liter surge tank U. The pressure regulator consisted simply of a tube immersed in a tank containing water, and regulation of the valve at the top of the tube varied the amount of air by-passed against a predetermined head of water.

For work above 0 C, the bath containing the vaporization coil was filled with water and manual temperature regulation was employed using the electrical immersion heater F (fig. 2). At temperatures below 0 C, and in some of the later experiments above 0 C, the bath liquid consisted of a mixture in equal parts of carbon tetrachloride and gasoline. The temperature was automatically controlled by means of a mercury-in-glass thermoregulator V (fig. 3), the excess cooling by means of a carbon dioxide expansion coil W being compensated for by the addition of electrical energy through the heating coil F. In some of the earlier experiments, a mixture of finely shaved ice and water was used to obtain a temperature of 0 C.

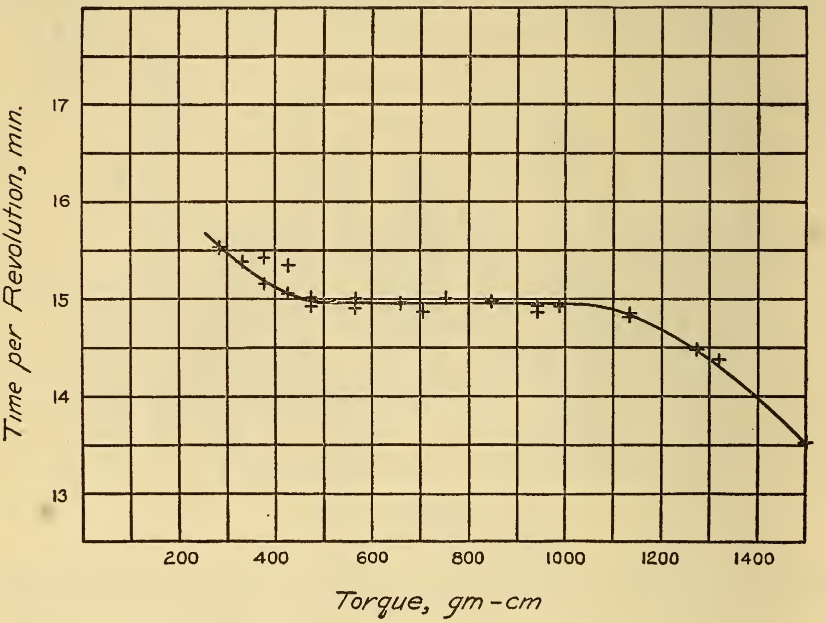

Figure 4.—*Calibration curve for mechanism controlling rate of gasoline feed.*

2. CALIBRATION OF APPARATUS

(a) CALIBRATION OF GASOLINE DISPLACEMENT SYSTEM

The volume of gasoline supplied to the vaporization coil is dependent upon the displacement of the plunger, upon the size of the drum on the clock spindle, and upon the clock rate. The plunger was a uniform cylinder of outside diameter 2.540 cm and displacement 5.067 ml per cm immersion. The clock rate was checked for a wide range of weights with each of the four drums. For each measurement, the torque was computed by multiplying the weight of the plunger in grams by the effective radius of the drum in centimeters. The effective radius was taken to be the actual radius plus that of the wire. The calibration data are shown in graphical form in figure 4, in which the time per revolution, in minutes, is plotted against the torque in g–cm. Over a considerable range, the clock rate is constant, but the departure from constancy is very marked toward each end of the curve.

Appropriate weights for each drum were computed from the torque required for the same clock rate in all cases, namely, one revolution in 14.95 minutes. In choosing these values, allowance was made for the decrease in torque due to increasing loss of weight with depth of immersion. For example, no. 2 drum had an effective radius of 0.943 cm and with a plunger weighing 1,000 g, the torque equals 943 g–cm and the clock rate is 14.95 min per revolution. The weight of the plunger would have to drop below 500 g before the clock rate is affected. If the plunger were immersed to a depth of 25 cm, the volume displaced would be 126.7 ml and the loss in weight due to buoyancy in a gasoline having a 60 F/60 F specific gravity of 0.720 would be 91.2 g. This change in weight would not affect the clock rate and therefore a plunger weight of 1,000 g is appropriate for use with no. 2 drum. Adjustment of the plunger weight with the different drums was accomplished by means of lead shot put into or withdrawn from the interior of the plunger. In some cases a second wire was wound around the drum and thence over an idler pulley to a weight to supply an additional load on the drum.

The volume of gasoline F displaced per unit time, expressed in milliliters per minute, is

$$F=k\pi DrA \qquad (1)$$

where D is the effective diameter of the drum in centimeters, r is the clock rate in rpm, A is the displacement in milliliters per centimeter length of the plunger, while k is a constant equal to 1.000027, to transform from cubic centimeters to milliliters, and π equals 3.1416. With the present apparatus, $r=1/14.95$, and $A=5.067$, so that the relation in equation 1 becomes

$$F=1.065D \qquad (1A)$$

The data on the four drums are given in table 3.

TABLE 3.—*Constants of the drums used in the gasoline displacement system*

Number	Effective diameter	Gasoline displacement		Weight on drum
	cm	*ml/rev*	*ml/min*	*g*
1	0. 943	15	1. 003	1, 500
2	1. 885	30	2. 006	1, 000
3	2. 827	45	3. 010	500
4	3. 769	60	4. 013	500

The weight of gasoline displaced per unit time is the product of the volume and the density of the gasoline at the temperature existing in the reservoir H at the time of displacement. Hence

$$W_g=Fd \qquad (2)$$

where W_g is the weight of gasoline in grams per minute and d is the density. Values of the density at the desired temperatures were obtained from the measured gravity at 60 F making use of the national standard petroleum oil tables,[4] for the change of density with temperature.

(b) CALIBRATION OF FLOWMETER

The orifices used in the flowmeter were calibrated by comparison with a master orifice of known characteristics. The flow of air W_a in grams per minute is given by the formula

$$W_a = k\sqrt{H} \tag{3}$$

where k is the orifice constant for air at 25 C and 760 mm pressure, and H is the pressure drop across the orifice, expressed in centimeters of water. Within the experimental error of the volatility measurements k can be considered constant, since the variations in air temperature and pressure were small. Data on the five orifices used are given in table 4.

TABLE 4.—*Constants of the orifices used in the flowmeter*

Number	Approximate orifice diameter	Orifice constant
	Inch	
1	1/16	1.12
2	3/32	2.25
3	1/8	4.66
4	5/32	7.11
5	3/16	10.58

The pressure drop H across the orifice to give any desired air-fuel mixture for a specific rate of gasoline feed is obtained by combining equations 2 and 3, which leads to the relation

$$H = \left(\frac{M_s F d}{k}\right)^2 \tag{4}$$

where M_s is the supplied air-fuel mixture and is equal to W_a/W_g. The pressure drop H is the difference in level, in centimeters of water, between the two arms of the manometer across the orifice.

(c) CALIBRATION OF VAPORIZATION COIL

The degree of vaporization under flow conditions is a function not only of the thermodynamic variables, temperature, pressure and mixture ratio, but also in general a function of the rate of flow and the characteristics of the specific apparatus used. Hence, for vaporization data by a dynamic method to be general and a function of the thermodynamic variables only, it is necessary that the apparatus be calibrated to evaluate the effect of the rate of flow on the measurements. With a well-designed apparatus, carefully manipulated, the amount of liquid evaporated into the air stream from a constant supplied air-fuel mixture will vary continuously with the rate of flow through the vaporization coil, and the change in the amount evaporated with rate of flow will become successively less as the flow decreases. The value approached with each constant mixture and temperature as the rate of flow becomes zero is the equilibrium percentage evaporated. Hence if the percentages evaporated are measured for a number of sufficiently slow rates, which are determined by the particular apparatus, the extrapolated value at zero rate of flow is independent of the apparatus and represents the equilibrium value for vaporization from the specific mixture being studied at the specific temperature. Measurements with other mixtures and at a number of temperatures serve to establish the departure from equilibrium with this specific fuel under all conditions of use in the apparatus. Similar investigations with other fuels are necessary to determine whether a general relation for departure from equilibrium can be obtained which is independent of the particular fuel used.

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[4] N.B.S. Miscellaneous Publication No. 154, 1924.

An experimental investigation was made of the effect of temperature and mixture ratio on the change in the percentage evaporated with rate of gasoline flow in the case of a number of gasolines. Temperatures ranging from +45 to −30 C were employed and air-fuel mixtures from 0.5:1 to 16:1 were supplied to the vaporization coil. Experiments were made with 5 fuels and rates of gasoline feed of 1, 2, 3, and 4 ml per min were used. Under each set of conditions, the values of the amounts evaporated, expressed in weight percent, were plotted against the rate of gasoline feed and the line through these points was extrapolated to zero rate of feed. This extrapolated value was considered to be the equilibrium percentage evaporated.

A study of the data showed that the departure from equilibrium vaporization was independent of the specific fuel, the temperature and the supplied air-fuel mixture, and was dependent only upon the rate of feed and the percentage evaporated. The following relation was found to hold for all of the measurements:

$$P = P_o(1 + 0.0125F) \tag{5}$$

where P is the equilibrium percentage evaporated and P_o is the experimentally determined value at the feed F in milliliters per minute.

The departure from equilibrium vaporization is illustrated graphically in figure 5, in which deviations from equation 5 are plotted against P employing different symbols for the four rates of gasoline feed used, approximately 1, 2, 3, and 4 ml per min. The agreement of the data with equation 5 is further illustrated in table 5 for fuels $B3$ and 111, in which are recorded values of P at various temperatures and with a number of supplied air-fuel mixtures. The values of P were computed from the experimental values of percentages evaporated P_o by means of equation 5 and hence if the equation is valid, P should be constant at each temperature and with each mixture. The deviations from constancy are listed in the table and no trend of the deviations with either temperature or mixture ratio is noted. The grand average deviation from equation 5 is 1 percent evaporated. At small percentages evaporated, the departure from equilibrium vaporization is less than the average deviation from the equation, so that in this range, the results indicate the degree of reproducibility of the measurements, which is one unit in the percentage evaporated.

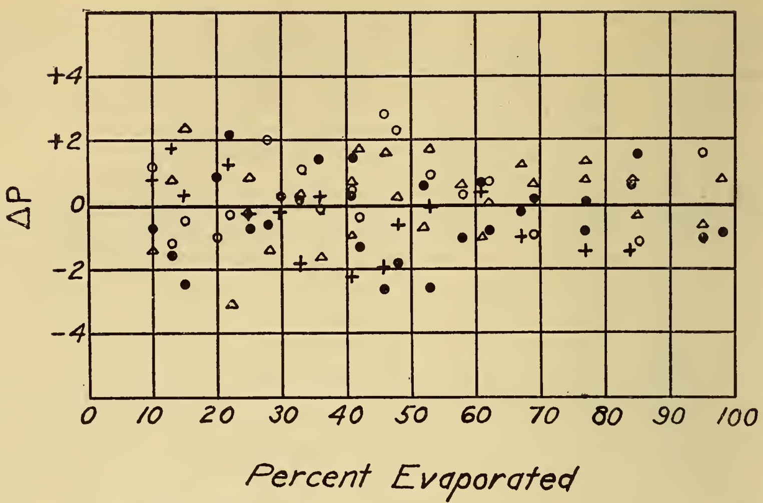

FIGURE 5.—*Deviation plot showing lack of trend in deviations from equation 5.*

TABLE 5.—*Test of equation 5 for correction to equilibrium vaporization*

(1) DATA FOR FUEL B3

Feed	P for M_s=4	ΔP	P for M_s=8	ΔP	P for M_s=12	ΔP	P for M_s=16	ΔP
(*a*) TEMPERATURE=15 C								
1.003	47.2	−0.6	66.2	−1.0	75.7	−1.4	82.1	−1.4
2.006	46.0	−1.8	67.0	−.2	77.2	+.1	84.1	+.6
3.010	48.1	+.3	68.5	+1.3	78.5	+1.4	84.3	+.8
4.013	50.1	+2.3						
Average	47.8	±1.3	67.2	±.8	77.1	±1.0	83.5	±.9
(*b*) TEMPERATURE=0 C								
1.003	36.1	+0.3	43.6	−1.9	53.2	0.0	61.1	+0.4
2.006	37.3	+1.5	42.9	−2.6	50.6	−2.6	61.4	+.7
3.010	34.2	−1.6	47.2	+1.7	55.0	+1.8	59.7	−1.0
4.013	35.7	−.1	48.3	+2.8	54.1	+.9		
Average	35.8	±.9	45.5	±2.2	53.2	±1.3	60.7	±.7
(*c*) TEMPERATURE=−15 C								
1.003	14.8	+1.8	24.6	−0.2	31.6	−1.8	38.4	−2.2
2.006	11.5	−1.5	24.1	−.7	33.6	+.2	42.1	+1.5
3.010	13.8	+.8	25.7	+.9	33.7	+.3	41.4	+.8
4.013	11.8	−1.2	24.6	−.2	34.5	+1.1		
Average	13.0	±1.3	24.8	±.5	33.4	+.6	40.6	±1.5
(*d*) TEMPERATURE=−30 C								
1.003	10.3	+0.8	15.4	+0.3	23.0	+1.3	30.0	−0.2
2.006	8.8	−.7	12.7	−2.4	23.9	+2.2	30.5	+.3
3.010	8.1	−1.4	17.5	+2.4	18.6	−3.1		
4,013	10.7	+1.2	14.6	−.5	21.4	−.3		
Average	9.5	±1.0	15.1	±1.4	21.7	±1.7	30.2	±.3

Grand average deviation=±1.1.

TABLE 5.—*Test of equation 5 for correction to equilibrium vaporization*—Continued

(2) DATA FOR FUEL 111

Feed	P for $M_s=4$	ΔP	P for $M_s=8$	ΔP	P for $M_s=12$	ΔP	P for $M_s=16$	ΔP
(*a*) TEMPERATURE=0 C								
2.006	61.3	−0.8	86.5	±1.6	94.2	−1.1	96.8	−0.9
3.010	62.2	+.1	84.6	−.3	94.7	−.6	98.5	+.8
4.013	62.8	+.7	83.7	−1.2	96.9	+1.6		
Average	62.1	±.5	84.9	±1.0	95.3	±1.1	97.7	±.9
(*b*) TEMPERATURE=−15 C								
2.006	40.6	−1.3	57.3	−1.0	69.2	+0.2	76.6	−0.8
3.010	43.7	+1.8	59.0	+.7	69.7	+.7	78.2	+.8
4.013	41.5	−.4	58.6	+.3	68.0	−1.0		
Average	41.9	±1.1	58.3	±.7	69.0	±.6	77.4	±.8
(*c*) TEMPERATURE=−30 C								
2.006	20.8	+0.9	27.3	−0.6	41.6	+0.3	52.1	+0.6
3.010			26.5	−1.4	40.4	−.9	50.8	−.7
4.013	18.9	−1.0	29.9	+2.0	41.8	+.5		
Average	19.9	±1.0	27.9	±1.3	41.3	±.6	51.5	±.7

Grand average deviation=±0.9.

Verification of the conclusion that the corrected experimental results represent equilibrium conditions, was obtained by experiments on pure toluene. In this case, the known molecular weight and vapor pressure data permit a computation of the volatility. Determinations were made with a considerable number of supplied air-toluene mixtures and at the four temperatures 0, 15, 25, and 35 C. From the plot of these experimental data, the temperatures corresponding to four resultant air-vapor mixtures covering the range of interest were obtained and a comparison is made in table 6 with the calculated temperatures. The details of this procedure for obtaining both the experimental and calculated values will be explained later in this paper. The agreement between the two sets of values substantiates the conclusion that, within the experimental error of the measurements, the corrected results obtained with the Sligh volatility apparatus closely approximate equilibrium conditions.

TABLE 6.—*Comparison of observed and calculated temperatures for various resultant mixtures of air and toluene vapor*

Mixture	Observed temperature	Calculated temperature
	° *C*	° *C*
8:1	23	25
12:1	17	17
16:1	12	12
20:1	8	8

All values obtained in the study of fuel volatility were corrected to equilibrium values by means of equation 5.

3. GENERAL EXPERIMENTAL PROCEDURE

The method of using the equilibrium air-evaporation apparatus is comparatively simple. In making an experiment, the drum on the clock spindle was rotated so as to raise the plunger to the top of the reservoir, which was then filled with the gasoline. For most purposes, the 2 or 3 ml per min drums were found to be the most convenient. After the temperature of the bath was adjusted, the air supply was turned on, the manometer head was regulated to the value computed from equation 4 for the desired air-fuel mixture and the clock was started. A few minutes were allowed for constancy to be attained and measurements were then made of the amount unvaporized. After several check readings, the experimental conditions were varied and other readings were taken. With each fuel, a sufficient number of supplied mixtures were employed over a range of temperature to cover the desired volatility field.

In determining the volume of gasoline unvaporized, two different sizes of burettes were found to be convenient. For large amounts unvaporized, the volume collected per unit time was large and a burette of 5 ml capacity was used; whereas, for small amounts unvaporized, one of 1 ml capacity was employed. Drainage errors in the burette were avoided by starting a stop watch when the liquid passed a given mark, by draining the gasoline into a calibrated flask of 1 or 5 ml capacity until full and then stopping the watch when the meniscus passed the mark on the burette a second time. The accuracy of the stop watch was checked periodically.

It is necessary to know the specific gravities of the original fuel and of the residual liquid after partial vaporization, in order to express the experimental results on a weight basis. Accordingly, the specific gravities of the original gasoline and of each residue were determined at 60 F. by means of a pycnometer. The gravities at other temperatures were obtained from the national standard petroleum oil tables.[5]

The percentage by weight of gasoline evaporated during an experiment is given by the relation

$$P_0=\frac{Fd_1-Vd_2}{Fd_1}\times 100 \tag{6}$$

where F is the volume of liquid in milliliters supplied per minute, computed from equation $1A$; d_1 is the specific gravity of the original gasoline at room temperature; V is the measured volume of the liquid residue collected per minute; and d_2 is the specific gravity of the residue at the temperature of the bath containing the vaporization coil. It has been found that the small difference in temperature between the residue collected in the burette and that in the bath introduces a negligible error. In every case the values of P_0 were corrected to equilibrium values by means of equation 5.

A sample data sheet indicating the details of computation is shown in table 7.

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[5] See reference 4.

TABLE 7.—*Sample data sheet — fuel S3*

Temperature	Supplied mixture M_s	Feed F	Orifice size	Pressure drop H	Specific gravity of residue		Time for collection of 1 ml of residue	Obs. weight percent evaporated, P_o	Corr. to equilibrium, vaporization	Equilibrium wt percent evaporated, P
					60 F/60 F	t°/160 F				
° *C*			*Inch*				*Sec.*			
15	4	3.010	1/8	3.5	0.765	0.765	37.6	43.9	1.6	45.5
	8	3.010	5/32	6.0	.772	.772	53.3	60.1	2.3	62.4
	12	3.010	3/16	6.0	.777	.777	65.4	67.2	2.5	69.7
	16	2.006	5/32	10.6	.782	.782	123.6	73.8	1.8	75.6
0	4	3.010	1/8	3.5	.755	.767	30.2	29.9	1.1	31.0
	8	3.010	5/32	6.0	.763	.775	35.2	39.3	1.5	40.8
	12	3.010	3/16	6.0	.765	.777	42.8	49.9	1.9	51.8
	16	2.006	5/32	10.6	.771	.783	72.0	55.0	1.4	45.4
−15	4	3.010	1/8	3.5	.749	.773	27.4	22.2	.8	23.0
	8	3.010	5/32	6.0	.754	.778	29.0	26.0	1.0	27.0
	12	3.010	3/16	6.0	.758	.782	32.8	34.3	1.3	35.6
	16	2.006	5/32	10.6	.763	.786	52.2	37.7	.9	38.6
−30	4	3.010	1/8	3.5	.739	.776	24.2	11.5	.4	11.9
	8	3.010	5/32	6.0	.744	.780	26.0	17.3	.6	17.9
	12	3.010	3/16	6.0	.750	.786	26.9	19.4	.7	20.1
	16	2.006	5/32	10.6	.755	.791	43.0	23.9	.6	24.5

Specific gravity of original gasoline (77 F/60 F) = 0.723.

VI. METHOD OF TREATMENT OF EXPERIMENTAL DATA

1. PARTIAL VOLATILITY AND DEW-POINT DATA

In the preliminary treatment of the experimental data, values of the volatility, in terms of the temperature required to produce a given resultant air-vapor mixture, were obtained graphically for each such resultant mixture. The corrected percentages evaporated were plotted against the corrresponding temperatures for each supplied air-fuel mixture and smooth curves were drawn through the points. This gave a temperature-percentage evaporated curve for every supplied mixture. The percentage evaporated P which would produce a given resultant air-vapor mixture M_R from each supplied mixture M_S was computed by means of the relation

$$P = \frac{M_S}{0.01\ M_R} \tag{7}$$

Values of P thus computed were used to locate temperatures on the supplied mixture curves, corresponding to the various resultant mixtures of interest. Smooth curves were then put through these points, so that a temperature-percentage evaporated curve was obtained for each desired resultant air-vapor mixture.

A sample diagram is shown in figure 6 for fuel S1. The circles represent the experimentally observed values corrected to equilibrium by means of equation 5. The continuous lines through these points correspond to the four supplied air-fuel mixtures of 4:1, 8:1, 12:1, and 16:1. The dotted lines indicate temperatures along resultant air-vapor mixture lines of 8:1, 12:1, 16:1, and 20:1. From equation 7, it is found that a 20:1 resultant mixture will be formed from a 16:1 supplied mixture when 80 percent of the fuel is evaporated. The same resultant mixture will be formed from an 8:1 supplied mixture at 40 percent evaporated and from a 4:1 mixture at 20 percent evaporated. By drawing a smooth curve through these points corresponding to the same resultant mixture, it is possible to determine the temperatures at various percentages evaporated which will produce this constant air-vapor mixture. Thus at 80 percent evaporated, a temperature of 24 C is required to produce a 20:1 air-vapor mixture. At temperatures below this, at the same percentage evaporated, leaner mixtures are formed; at higher temperatures, the resultant mixtures are richer.

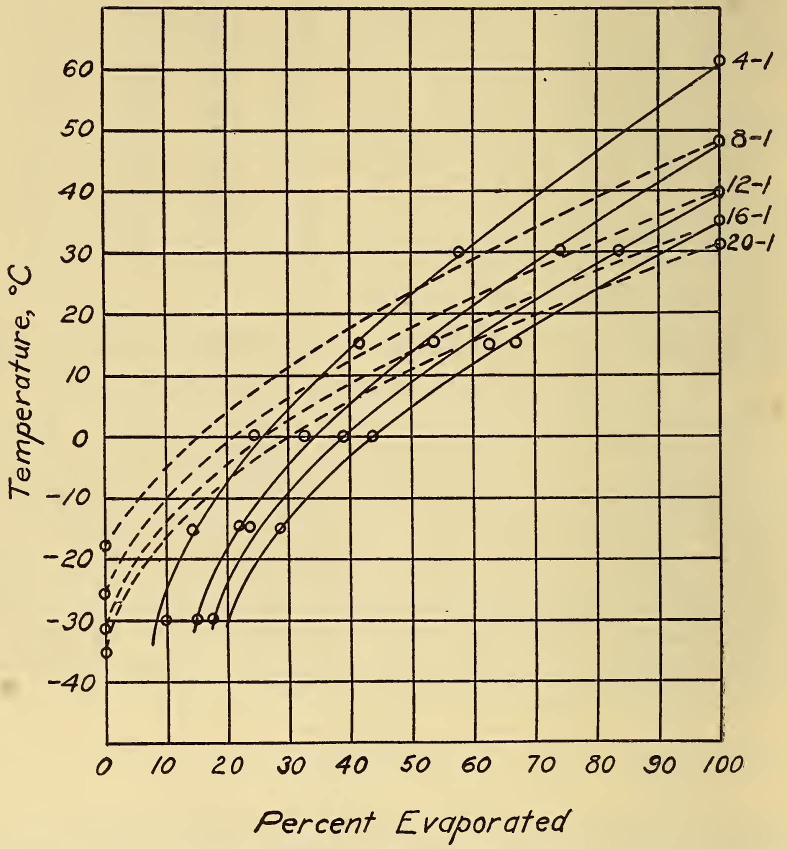

Figure 6.—*Volatility curves for fuel S1. The solid lines correspond to designated air-liquid fuel ratios, while the dashed lines correspond to designated air-vapor ratios.*

The dew points of the various mixtures are the intercepts of the extrapolated mixture lines with the vertical line of 100 percent evaporated. Each intercept is rendered more certain by the fact that analogous supplied and resultant mixture lines must intersect at the dew point, which essentially amounts to a double smoothing of the data, thereby increasing the accuracy. Thus, with reference to figure 6, the continuous and dotted lines for 16:1 supplied and resultant mixtures respectively cross at 100 percent evaporated at a temperature of 35 C, which is the 16:1 dew point of this gasoline.

Plots similar to that shown in figure 6 were made for each fuel studied. The evaluation of the bubble points of these mixtures will be discussed in the following section.

While the method outlined was fairly satisfactory for the evaluation of the volatility data from the experimental results, two graphical smoothings of the data were involved and there was some latitude for personal judgment in drawing the curves. Accordingly, it was considered desirable to develop a method in which all of the points on each fuel would be considered simultaneously in drawing any one line. Inspection of the original curves for the entire set of data on the 38 fuels showed that the difference in temperature between any two resultant mixtures lines from 8:1 to 20:1 was the same at every percentage evaporated and for each gasoline studied, the average deviation from constancy being considerably less than 1° C.

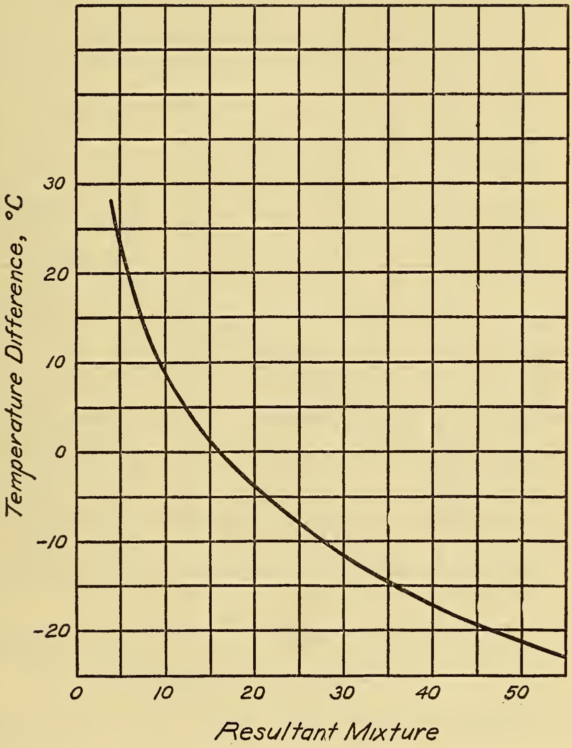

Figure 7.—*Curve showing differences in temperature between lines for various resultant air-vapor mixtures.*

The differences in temperature between various resultant air-vapor mixture lines are shown in figure 7, referred to a 16:1 mixture as standard. Thus, if the temperature on a 16:1 mixture line at 90 percent evaporated is 40 C, the temperature on a 20:1 line at the same percentage evaporated will be obtained by adding −4° C, giving 36 C. On the other hand, if the 16:1 temperature at 10 percent evaporated is −20 C, the 8:1 temperature at 10 percent evaporated will be (−20+13) °C or −7 C. Values for other mixtures at any percentage evaporated can be obtained in a similar manner.

The constant temperature difference between any two resultant mixture lines, over the range of interest, made it possible to transform all of the data on any one gasoline to temperatures along a 16:1 resultant mixture line. Thus, for each experimental value of supplied mixture and percentage evaporated, the value of the resultant mixture formed was computed from equation 7. Then by means of the curve in figure 7, the experimental temperature to which the above data apply was corrected to the value corresponding to the 16:1 resultant mixture at the same percentage evaporated. For example, assume that the equilibrium percentage evaporated is 80 percent at 50 C when supplying a 16:1 air-fuel mixture. From equation 7 the resultant air-vapor mixture, M_R equals 20:1, and from the curve in figure 7, the temperature difference between a 20:1 and a 16:1 resultant air-vapor mixture is 4° C. Therefore at 80 percent evaporated, a 16:1 resultant mixture would be formed at $50-4°\ C=46$ C.

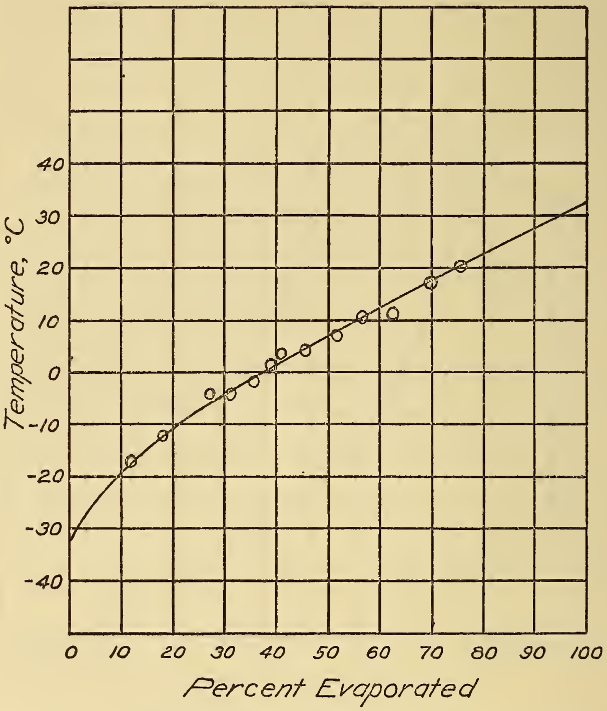

Figure 8.—*Volatility curve for resultant mixture containing 16 parts of air and 1 part of fuel S3 by weight.*

Temperatures, thus corrected to values on a 16:1 resultant mixture line, were plotted against the corresponding percentages evaporated and a smooth curve was drawn through these points. An example is shown in figure 8 for fuel S3. The value at 0 percent evaporated was obtained in a manner described in the following section. Similar curves were drawn for the 38 fuels and the temperatures at every 10 percent evaporated from 10 to 100 percent inclusive read from these curves are shown in table 8. The values from 10 to 90 percent represent partial volatility data while the temperatures at 100 percent evaporated represent dew points. The dew-point values for fuels 1A, 2A, 3A, and 4A are in parentheses, because these values were obtained by extrapolation over a much longer range than usual.

TABLE 8.—*16:1 temperatures from experimental curves, °C at stated percentages evaporated*

Fuel	10	20	30	40	50	60	70	80	90	100
1	15	23	29	34	39	43	48	51	55	59
3	4	19	29	35	40	44	47	50	53	56
1A	−5	5	13	20	27	33	38	44	49	(54)
2A	−1	8	16	23	29	34	39	44	49	(53)
3A	1	10	17	23	29	34	39	44	48	(53)
4A	2	11	18	23	29	33	37	41	45	(49)
A	−8	5	15	20	25	31	36	43	49	56
B	−17	−8	−4	−1	1	4	6	9	11	14
C	−13	−3	4	9	13	17	22	27	33	40
D	2	8	12	15	17	20	25	33	45	57
E	−2	9	17	22	27	33	39	45	51	58
F	−10	10	26	36	42	46	50	52	55	57
RH	−3	5	11	16	20	24	27	31	34	37
L	17	18	19	20	21	22	23	24	25	27
RPC	−15	−1	10	19	27	34	40	47	53	59
2	−20	−12	−5	2	9	17	26	36	46	56
6	5	12	18	22	27	32	36	41	47	53
G	−2	0	2	5	8	12	17	24	24	44
H	−11	−3	4	9	14	20	27	34	42	50
I	−10	−6	−5	−4	0	6	14	23	33	44
J	−22	−7	6	16	26	34	42	50	58	65
K	−15	−4	4	11	17	23	28	33	38	42
M	2	16	26	32	38	45	52	59	67	75
N	7	17	24	31	38	43	49	54	59	64
O	−2	11	20	28	35	41	47	52	58	63
B3	−15	−9	−4	0	5	9	13	16	20	24
101	−34	−31	−29	−26	−24	−21	−18	−14	−10	−4
111	−26	−24	−22	−20	−18	−16	−13	−10	−5	1
121	−14	−13	−12	−12	−11	−10	−8	−6	−4	−1
S1	−15	−6	2	8	13	18	23	27	31	35
S2	−15	−7	0	6	11	16	21	26	31	35
S3	−19	−11	−5	0	6	11	17	22	28	34
S4	−23	−14	−7	−1	4	10	15	21	27	33
S5	−26	−17	−10	−4	1	6	12	13	25	31
S6	−30	−23	−19	−14	−8	−2	5	12	20	28
EB1	−30	−27	−23	−18	−12	−4	1	5	8	10
EB2	−35	−34	−33	−31	−29	−24	−17	−6	2	8
EB3	−38	−38	−38	−38	−37	−37	−36	−32	−9	0

A 16:1 air-vapor mixture was chosen as a standard of reference since it is essentially the leanest mixture which it is feasible to employ in the engine. However, the method works equally well for other reference mixtures from 4:1 to 20:1, which covers the range of interest in automotive work.

2. BUBBLE-POINT DATA

When the curve representing any given air-vapor mixture is extrapolated back to cut the vertical line of 0 percent evaporated, the point of intersection is the bubble point and represents the limiting temperature below which this given mixture cannot be formed. In general, the determination of bubble points of air-vapor mixtures by extrapolation of these equilibrium air-evaporation curves is not feasible, due to increasing curvature at smaller percentages evaporated. Bubble points may, however, be computed from the vapor pressures of the gas-free gasolines over a range of temperatures and from the molecular weights of the hydrocarbon vapors present in the small bubbles which form in the gasolines at the bubble points. Direct determination of the molecular weights of the vapors formed under these conditions is difficult so an indirect method was employed involving computation from measurements of the molecular weights of the liquid residues at various percentages evaporated obtained by means of the equilibrium air-evaporation apparatus.

From the 16:1 air-vapor curves of the fuels studied, the temperatures were read at 20, 40, 60, and 80 percent evaporated. Then using equation 7, the air-fuel mixtures which must be supplied in each case to produce a 16:1 resultant mixture were computed. With every fuel, each computed air-fuel mixture was run through the equilibrium air-evaporation apparatus at the appropriate temperature to give the desired resultant mixture at the chosen percentage evaporated. About 50 ml of residue was collected under each set of conditions and the molecular weights of these samples and of the original gasolines were determined by measuring the lowerings in the freezing point of pure benzene on addition of known amounts of the residues.[6] These data were then plotted against the percentage evaporated and a smooth curve drawn through the plotted points, as illustrated in the upper curve of figure 9 for fuel A. From this curve, the molecular weights were obtained at 5 percent evaporated and thereafter at every 10 percent evaporated up to 60 or 80 percent, and were used to compute the molecular weights of the vapors formed under each set of conditions.

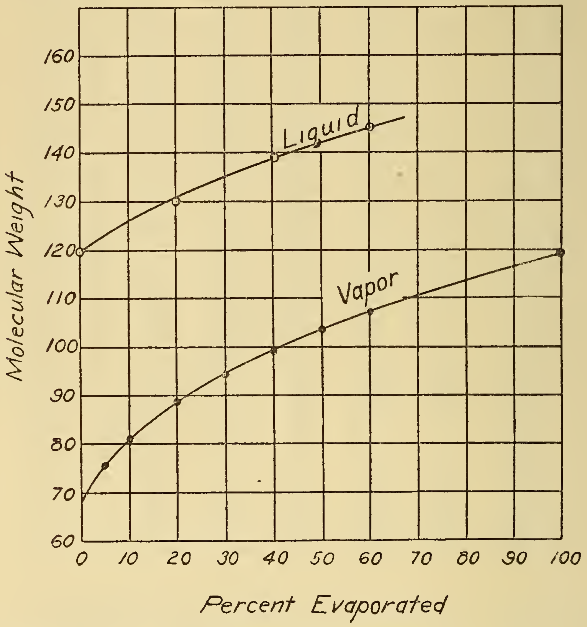

Figure 9.—*Molecular weight curves of liquid and vapor for fuel A at various percentages evaporated.*

Since the number of moles of gasoline in the residue plus those of the vapor in the resultant mixture at any percentage evaporated are necessarily equal to the number of moles of gasoline supplied, it follows that

$$\frac{100-P}{M_L}+\frac{P}{M_F}=\frac{100}{M_G} \tag{8}$$

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[6] Bridgeman, SAE Jour., Nov. 1928, p. 478.

where P is the percentage evaporated by weight, and M_L, M_F, and M_G are the molecular weights, respectively, of the liquid residue, of the vaporized fuel, and of the original gasoline.

Rearranging equation 8, it becomes

$$M_F = \frac{M_L}{1+\frac{100}{P}\cdot\frac{\Delta M}{M_G}} \tag{9}$$

where $\Delta M = M_L - M_G$. For each value of the molecular weight of the residue, M_L, obtained from the curve, the corresponding value of the molecular weight of the gasoline vapor, M_F, at the same percentage evaporated, was computed from equation 9. For example, if the molecular weight of the original gasoline is 100 and the molecular weight of the residue at 50 percent evaporated is 120, then $\Delta M = 20$, and $M_F = 120/1.4 = 86$ at 50 percent evaporated.

The computed values of the molecular weights of the vapors were plotted against the percentage evaporated and a smooth curve was drawn through the points, as illustrated in the lower curve of figure 9. The extrapolated value at 0 percent evaporated is the desired molecular weight of the vapor in the first small bubble which forms in the gasoline under equilibrium conditions corresponding to a 16:1 resultant air-vapor mixture.

The next step is the determination of the bubble point temperature, which involves a knowledge of the gasoline vapor pressure necessary for the formation of a 16:1 resultant mixture. Assuming that both the gasoline vapor and the air obey the perfect gas laws, which is closely true, then

$$\frac{p_A}{p_F} = \frac{W_A M_F}{W_F M_A} \tag{10}$$

where p_A and p_F are the respective partial pressures of air and fuel vapor in the resultant mixture, expressed in millimeters of mercury; W_A and W_F are their respective masses in grams; and M_A and M_F are their respective molecular weights. Further, since the total pressure of the mixture is 760 mm of mercury

$$p_A = 760 - p_F. \tag{11}$$

Combining equations 10 and 11, and substituting the resultant mixture ratio M_R for W_A/W_F, there results

$$p_F = \frac{760}{1+M_R\cdot\frac{M_F}{M_A}}. \tag{12}$$

Substituting 16 for M_R and taking the molecular weight of air as 28.96, the relation becomes

$$p_F = \frac{760}{1+0.553 M_F}. \tag{13}$$

Using the molecular weights of the gasoline vapors, M_F, obtained from the extrapolated molecular weight curve for each fuel, the values of the vapor pressures of the gasolines, p_F, necessary to form 16:1 air-vapor mixtures in the small bubbles were computed from equation 13.

The last step involves the evaluation of the temperature with each gasoline at which the vapor pressure has the value computed above. For this purpose, the gasolines were dried and freed from dissolved gases and their vapor pressures were measured over a range of temperatures under conditions such that a small bubble of vapor was present in each case. The details of the methods used in the preparation of the gasoline samples and in the vapor-pressure measurements will be presented in a later paper.[7] It was found that the vapor-pressure data on each gasoline could be accurately reproduced by an equation of the form

$$\log_{10}\frac{p_F}{760}=A\left[1-\frac{T_n}{T}\right] \tag{14}$$

where T is the temperature in absolute centigrade degrees corresponding to the vapor pressure p_F in millimeters of mercury; T_n is the temperature in absolute centigrade degrees at which the vapor pressure is equal to 760 mm of mercury; and A is a specific constant evaluated from the data on each fuel. Using the values of p_F obtained from equation 13 and the appropriate values of the constant A, equation 14 was used to compute the desired bubble point temperatures $(T-273.1)$ corresponding to 16:1 resultant mixtures of air and vapor from the various gasolines.

An example for fuel A will illustrate the method of computation. From the curve of molecular weight of the vapor in the 16:1 resultant air-vapor mixture, the value of the molecular weight at 0 percent evaporated is found on extrapolation to be 68. Substituting this value for M_F in equation 13, the partial pressure p_F of gasoline vapor in the mixture is computed to be 19.7 mm of mercury. From vapor pressure measurements on this fuel, the temperature at which the vapor pressure equals 760 mm is 74.0 C, and the constant A equals 3.87. T_n is therefore $74.0+273.1=347.1$ K. Substituting these values for p_F, T_n and A in equation 14, T is found to be 246 K. The desired bubble point is then equal to $246-273=-27$ C.

Molecular weight and vapor pressure data were obtained on 5 gasolines and their 16:1 bubble points evaluated in the manner indicated are given in table 9.

TABLE 9.—*Evaluation of 16:1 bubble points*

Fuel	Molecular weight of vapor for 16:1 mixture, M_F	Partial pressure of gasoline vapor, p_F	Normal bubble point	Vapor pressure constant A	16:1 bubble point
			°C		°C
A	68	19.7	74.0	3.87	−27
B	68	19.7	63.0	3.97	−33
C	68	19.7	68.7	3.96	−29
J	66	20.3	55.4	3.84	−40
M	76	17.7	88.7	3.96	−16

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[7] Preliminary information is given by Bridgeman, Aldrich, and White, SAE Jour., p. 488, May 1929; and A.P.I. Bull., section 3, p. 4, Jan. 2, 1930.

VII. CORRELATION OF VOLATILITY DATA WITH A.S.T.M. DISTILLATION DATA

1. PRELIMINARY METHOD OF CORRELATION[8]

Although the equilibrium air-evaporation apparatus seems to be satisfactory for the determination of gasoline volatility, nevertheless it is not convenient for testing a large number of gasolines rapidly, due to the time required in obtaining complete information on each sample. On the other hand, the A.S.T.M. distillation test is simple, reproducible and in common use, so that an attempt was made to interpret the A.S.T.M. evaporation curves in terms of volatility, on the basis of the data obtained on the 38 diverse fuels.

A scheme of correlation of the results obtained by the two methods is suggested by the Clapeyron equation for pure substances which is

$$\frac{dp_F}{dT}=\frac{L}{T(V_1-V_2)} \tag{15}$$

where p_F is the vapor pressure at the temperature T in absolute degrees; L is the latent heat of vaporization per mole; V_1 is the molal volume of the vapor and V_2 is the molal volume of the liquid.

For the conditions involved in the present work, where the pressure is below atmospheric, the volume of the liquid is negligible in comparison with that of the vapor and it can be assumed without much error that the vapor obeys the perfect gas law, namely, $p_FV_1=RT$, where R is the gas constant per mole. Under these conditions, the Clapeyron equation 15 becomes

$$\frac{1}{p_F}\cdot\frac{dp_F}{dT}=\frac{L}{RT^2} \tag{16}$$

Integration yields the relation

$$\log_e\frac{p_F}{760}=\frac{L}{RT_n}\left[1-\frac{T_n}{T}\right] \tag{17}$$

where L is assumed to be independent of temperature and T_n is the boiling point in absolute degrees corresponding to a pressure of 760 mm of mercury. Experimental evidence has shown that L/RT_n has approximately the same value for substances like the hydrocarbons, which have similar properties, so that it can be replaced by the symbol a. In this case, equation 17 becomes

$$\log_e\frac{p_F}{760}=a\left[1-\frac{T_n}{T}\right] \tag{18}$$

If a mixture of hydrocarbon vapor and air in a space of volume V are both assumed to obey the perfect gas law, then

$$p_A=W_ART/M_AV \tag{19}$$

and

$$p_F=W_FRT/M_FV \tag{20}$$

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[8] See reference 3; also, Bridgeman, A.P.I. Bull., section 2, p. 124, Jan. 3, 1929; and SAE Jour., p. 137, August 1929.

where p_A and p_F are the respective partial pressures in millimeters of mercury of the air and hydrocarbon vapor in the mixture; W_A and W_F are their respective masses in grams; M_A and M_F are their respective molecular weights; V and T are the volume and absolute temperature of the mixture; and R is the gas constant per mole. Combination of equations 19 and 20 gives

$$\frac{p_A}{p_F}=\frac{W_A M_F}{W_F M_A} \tag{21}$$

Further, if the total pressure of the mixture is one atmosphere or 760 mm of mercury, then

$$p_A+p_F=760 \tag{22}$$

Substituting in equation 21 the value $(760-p_F)$ for p_A, and the mixture ratio M_R for W_A/W_F, there results

$$\frac{760}{p_F}=1+M_R\cdot\frac{M_F}{M_A} \tag{23}$$

Taking logarithms of both sides, equation 23 becomes

$$\log_e\frac{p_F}{760}=-\log_e\left[1+M_R\cdot\frac{M_F}{M_A}\right] \tag{24}$$

A combination of equations 18 and 24 gives

$$a\left[1-\frac{T_n}{T}\right]=-\log_e\left[1+M_R\cdot\frac{M_F}{M_A}\right]=-2.3\log_{10}\left[1+M_R\cdot\frac{M_F}{M_A}\right]$$

which on rearrangement becomes

$$\frac{T_n}{T}=1+\frac{2.3}{a}\log_{10}\left[1+M_R\cdot\frac{M_F}{M_A}\right] \tag{25}$$

The average molecular weight of the hydrocarbons in gasoline is about that of octane, namely 114, so that M_F can be replaced by $(114+\Delta M_F)$, where ΔM_F is the difference in molecular weight of octane and any other hydrocarbon which might be considered. The average molecular weight of air M_A is 28.96 and confining attention to a 16:1 resultant mixture M_R, equation 25 can be written

$$\frac{T_n}{T_{16}}=1+\frac{2.3}{a}\log_{10}\left[1+0.553(114+\Delta M_F)\right]$$

where T_{16} is the temperature in absolute degrees corresponding to a resultant 16:1 mixture.
Rearranging,

$$\frac{T_n}{T_{16}}=1+\frac{4.154}{a}+\frac{2.3}{a}\log_{10}(1+0.0086\Delta M_F)$$

For normal paraffin hydrocarbons, $2.3/a$ is approximately equal to 0.2 so that the equation becomes

$$\frac{T_n}{T_{16}}=1.36+0.2\log_{10}(1+0.0086\Delta M_F) \qquad (26)$$

The temperature ratio T_n/T_{16} in equation 26 is equal to 1.36 in the case of octane, since $\Delta M_F=0$. For nonane, $\Delta M_F=14$, in which case T_n/T_{16} equals 1.37. It is seen that T_n/T_{16} is essentially constant for hydrocarbons having a molecular weight close to that for octane and that the ratio is not very sensitive to changes in molecular weight.

With a group of similar gasolines, the molecular weights of the vapors in 16:1 mixtures should not be very different at the same percentage evaporated. Under these conditions, equation 26 suggests that the ratio of the absolute A.S.T.M. evaporation temperature to the absolute temperature of a 16:1 resultant mixture should be essentially constant at the same percentage evaporated. The ratios would, however, be different at each constant percentage evaporated. Accordingly, the ratio T_{ASTM}/T_{16} was evaluated for each of the 38 fuels at every 10 percent evaporated from 10 to 90 percent inclusive. At each constant percentage evaporated, the ratios were found to be approximately constant, as can be seen by comparing the average ratio at the bottom of the columns in table 11 with the observed values.

The correlation of dew point values with the A.S.T.M. data in the manner outlined above for partial volatility data is not feasible. It is impossible to obtain directly the temperature at 100 percent evaporated on the A.S.T.M. evaporation curve in the case of those gasolines which cannot be distilled dry, and it is impracticable to obtain this temperature by extrapolation due to the increasing curvature of the evaporation curve near the end point. Further, the temperatures recorded by the distillation thermometer near the end point are subject to considerably larger experimental error than are those between 10 and 90 percent evaporated. It was observed, however, that the 16:1 dew points were closely related to the temperatures at 90 percent evaporated on the A.S.T.M. evaporation curves. For each gasoline, the 90 percent point in absolute degrees was divided by the 16:1 dew point in absolute degrees and the ratios $T_{90\%}/T_{DP16}$ were found to be fairly constant, as can be seen from table 12, where the average ratio is given at the bottom of the column of observed ratios.

In correlating the bubble points with the A.S.T.M. data, the temperatures at 0 percent evaporated on the A.S.T.M. evaporation curves cannot, in general, be determined. There is ordinarily some distillation loss, so that the initial boiling point of the gasoline becomes the temperature at some percentage higher than 0 percent evaporated. Further, extrapolation to the temperature at 0 percent evaporated is not feasible, due to the increasing curvature at small percentages evaporated. Work on vapor pressures of gasolines indicated that there was a relation between the vapor pressure data and the A.S.T.M. evaporation temperatures at 10 percent evaporated, and this suggests an analogous relation for bubble points of 16:1 air-vapor mixtures. Accordingly, for each fuel the 10 percent point in degrees absolute was divided by the 16:1 bubble point in degrees absolute and the ratios $T_{10\%}/T_{BP16}$ were found to be very constant for the 5 fuels studied, as seen from table 13.

It should be pointed out that, while the A.S.T.M. and volatility data were compared at the same numerical percentages evaporated, the A.S.T.M. evaporation data are expressed in terms of volume percent, whereas the volatility data are expressed in terms of weight percent. The difference between the two types of percentage is appreciable, but not very large, and a correction to a common basis could be made if the density of the distillate in the A.S.T.M. tests were determined for a number of percentages evaporated. Since this requires additional experimentation and since each of the two types of percentage are in extensive use, the comparison was made in the somewhat illogical manner using the accepted variables, thereby permitting an interpretation of the A.S.T.M. evaporation curves directly in terms of the temperatures corresponding to various resultant air-vapor mixtures.

2. FINAL METHOD OF CORRELATION[9]

(a) GENERAL METHOD

A study of the temperature ratios showed that there was a trend with the volatility of the gasoline. Thus, for example, the ratios for a natural gas gasoline were lower than those for U.S. motor gasoline. This could be predicted from equation 25, for the molecular weights of the vapors from the two types of gasolines will differ considerably. Further, the constant a becomes smaller as the molecular weight M_F decreases. Equation 25 could be modified to take into account the variation of a with molecular weight in the case of pure hydrocarbons, but the application to the volatility data would be involved since the molecular weights of the vapors in air-gasoline mixtures are, in general, not known and their determination is difficult. Accordingly, a different type of relation was deduced for pure hydrocarbons.

From the data of Young[10] on the boiling points of pure hydrocarbons, use was made of the vapor pressure equation of Cragoe[11] to calculate the temperatures at which the vapor pressures corresponded in each case to a 16:1 air-vapor mixture, as given by equation 13. These data are tabulated in table 10. Values of $t_n - t_{16}$ were computed and it was found that these values could be expressed as a function of t_n by means of the equation $t_n - t_{16} = 65 + t_n/3$ which on arranging becomes

$$\frac{T_n}{T_{16}} = 1.5 - \frac{39}{T_{16}} \tag{27}$$

This equation relates temperature ratio and volatility, but does not take into consideration the fact that the distillation curve for a pure hydrocarbon is a straight horizontal line, while that for a gasoline in general shows curvature over the whole distillation range.

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[9] Briefly described by Bridgeman, SAE Jour., p. 345, October, 1929.

[10] Young, Proc. Royal Irish Acad., vol. 38, 65, 1928.

[11] Cragoe, Int. Crit. Tables, vol. 3, p. 228, 1928.

TABLE 10.—*16:1 Temperatures for pure hydrocarbons*

Hydrocarbon	Boiling point	16:1 temperatrue		Hydrocarbon	Boiling point	16:1 temperature	
		Cragoe equation	Equation 27			Cragoe equation	Equation 27
	°C	°C	°C		°C	°C	°C
C_4H_{10}	−1.0	−67	−66	C_9H_{20}	149.8	35	35
C_5H_{12}	36.1	−42	−41	$C_{10}H_{22}$	173.2	51	50
C_6H_{14}	68.8	−20	−19	$C_{11}H_{24}$	194.7	66	65
C_7H_{16}	98.4	0	1	$C_{12}H_{26}$	215.1	79	78
C_8H_{18}	125.3	19	18	$C_{13}H_{28}$	233.9	92	91

It seemed apparent that, in the limiting case of zero slope, a general relation for the temperature ratios of gasolines would reduce to equation 27. Thus, the relation for gasolines would be of the general form

$$\frac{T_{\text{ASTM}}}{T_{16}}=1.5-\frac{C}{T_{16}} \tag{28}$$

where C is a function of the slope of the A.S.T.M. evaporation curve and of the percentage evaporated, and reduces to 39 for pure hydrocarbons.

(b) APPLICATION TO PARTIAL VOLATILITY DATA

Analytical treatment of all of the partial volatility data on the 38 fuels showed that the parameter C of equation 28 could be expressed by means of the relation

$$C=\sqrt{460\ S}\ .\ \log_{10}\left[\frac{100-P}{50}\right]+39 \tag{29}$$

where S is the slope of the A.S.T.M. evaporation curve at any given percentage evaporated P. The slope is expressed in terms of degrees centigrade change per unit change in the percentage evaporated.

When $S=0$, the first term of equation 29 drops out leaving $C=39$, regardless of the percentage evaporated. This is the condition for pure hydrocarbons. When $P=50$, the first term again drops out leaving $C=39$, this time independent of the slope. This deduction from the equation appears to be accurately substantiated by the experimental data, namely, that with respect to temperature ratios over the range from 8:1 to 20:1 along a line of 50 percent evaporated, a gasoline behaves as if it were a pure hydrocarbon with a boiling point equal to the A.S.T.M. 50 percent point.

The slopes of the A.S.T.M. evaporation curve at every 10 percent evaporated from 10 to 90 percent were obtained for each fuel from the plotted curves, and the value of T_{ASTM}/T_{16} was computed for every point according to the relation in equations 28 and 29. These computed ratios are compared in table 11 with the ratios obtained from the experimental volatility data. The observed ratios are shown in the upper row of figures for each fuel and the computed ratios in the lower row.

TABLE 11.—*Comparison of observed and calculated temperature ratios for 16:1 mixtures*

Fuel number	For various percentages evaporated								
	10	20	30	40	50	60	70	80	90
1 [1]	1.344	1.348	1.355	1.365	1.372	1.383	1.390	1.407	1.439
	1.339	1.348	1.359	1.365	1.372	1.383	1.390	1.407	1.448
2	1.324	1.322	1.329	1.342	1.362	1.386	1.407	1.427	1.467
	1.319	1.326	1.333	1.342	1.357	1.372	1.394	1.418	1.454
3	1.314	1.340	1.358	1.370	1.377	1.385	1.396	1.412	1.442
	1.320	1.340	1.358	1.366	1.377	1.385	1.393	1.408	1.446
1A	1.318	1.341	1.354	1.365	1.373	1.383	1.395	1.414	1.454
	1.318	1.337	1.348	1.356	1.369	1.383	1.395	1.414	1.458
2A	1.313	1.341	1.350	1.355	1.364	1.379	1.395	1.414	1.454
	1.318	1.341	1.350	1.355	1.369	1.383	1.395	1.414	1.458
3A	1.335	1.350	1.355	1.361	1.368	1.381	1.395	1.414	1.451
	1.327	1.346	1.351	1.357	1.372	1.381	1.395	1.410	1.455
4A	1.320	1.348	1.358	1.368	1.368	1.383	1.396	1.414	1.444
	1.320	1.344	1.353	1.360	1.372	1.383	1.392	1.405	1.453
A	1.314	1.331	1.337	1.355	1.369	1.381	1.404	1.421	1.456
	1.314	1.331	1.342	1.355	1.369	1.377	1.396	1.417	1.452
B	1.312	1.325	1.338	1.349	1.365	1.371	1.384	1.394	1.426
	1.312	1.325	1.338	1.349	1.355	1.362	1.375	1.389	1.426
C	1.316	1.330	1.336	1.344	1.357	1.370	1.384	1.413	1.460
	1.316	1.330	1.341	1.349	1.361	1.370	1.384	1.413	1.460
D	1.317	1.334	1.344	1.351	1.363	1.366	1.370	(1.385)	1.487
	1.321	1.339	1.349	1.355	1.363	1.370	1.383	(1.418)	1.487
E	1.318	1.330	1.341	1.356	1.367	1.376	1.394	1.421	1.457
	1.318	1.335	1.350	1.360	1.367	1.376	1.394	1.417	1.457
F	1.312	1.322	1.338	1.362	1.384	1.398	1.400	1.409	1.436
	1.307	1.331	1.346	1.362	1.380	1.385	1.391	1.405	1.445
RH	1.326	1.338	1.345	1.353	1.362	1.370	1.386	1.401	1.436
	1.326	1.338	1.345	1.353	1.362	1.375	1.382	1.406	1.445
L	1.345	1.345	1.346	1.352	1.357	1.366	1.375	1.395	1.426
	1.349	1.355	1.355	1.361	1.361	1.370	1.375	1.395	1.436
6	1.313	1.330	1.340	1.359	1.374	1.384	1.398	1.414	1.448
	1.327	1.339	1.345	1.364	1.369	1.379	1.389	1.410	1.452
G	1.325	1.334	1.338	1.346	1.352	1.365	1.389	1.427	1.469
	1.329	1.338	1.343	1.350	1.357	1.365	1.389	1.414	1.460
H	1.321	1.329	1.329	1.330	1.345	1.365	1.390	1.424	1.457
	1.316	1.334	1.343	1.344	1.359	1.375	1.395	1.415	1.453
I	1.326	1.330	1.340	1.345	1.345	1.355	1.381	1.419	1.470
	1.322	1.335	1.340	1.345	1.349	1.360	1.385	1.419	1.461
RPC	1.314	1.320	1.332	1.343	1.356	1.368	1.390	1.416	1.445
	1.314	1.330	1.336	1.347	1.365	1.377	1.394	1.416	1.449
J	1.303	1.316	1.326	1.349	1.365	1.388	1.406	1.428	1.450
	1.303	1.321	1.340	1.349	1.369	1.379	1.402	1.415	1.446
K	1.310	1.327	1.339	1.352	1.362	1.371	1.389	1.409	1.444
	1.310	1.327	1.339	1.352	1.362	1.371	1.385	1.409	1.444
N	1.318	1.331	1.346	1.353	1.360	1.374	1.388	1.410	1.436
	1.327	1.340	1.351	1.357	1.374	1.378	1.397	1.414	1.441
O	1.310	1.320	1.335	1.349	1.364	1.379	1.394	1.412	1.429
	1.315	1.335	1.349	1.354	1.373	1.384	1.398	1.408	1.438
M	1.316	1.325	(1.335)	1.351	1.367	1.377	1.398	1.422	1.456
	1.320	1.339	(1.348)	1.355	1.371	1.381	1.398	1.422	1.465
B3	1.310	1.326	1.341	1.355	1.361	1.369	1.381	1.405	1.437
	1.306	1.326	1.337	1.346	1.361	1.369	1.381	1.405	1.441
101	1.318	1.322	1.328	1.328	1.341	1.353	1.372	1.397	1.441
	1.312	1.322	1.322	1.332	1.341	1.353	1.368	1.393	1.441
111	1.320	1.321	1.326	1.332	1.346	1.362	1.380	1.406	1.448
	1,320	1.320	1.332	1.337	1.346	1.356	1.371	1.392	1.442
121	1.332	1.334	1.337	1.340	1.344	1.350	1.359	1.379	1.425
	1.328	1.334	1.341	1.340	1.344	1.350	1.364	1.385	1.439
S1	1.306	1.322	1.335	1.341	1.356	1.375	1.389	1.414	1.440
	1.310	1.322	1.339	1.345	1.360	1.371	1.389	1.410	1.436
S2	1.306	1.323	1.332	1.348	1.362	1.376	1.394	1.418	1.444
	1.310	1.323	1.332	1.348	1.362	1.372	1.390	1.409	1.444
S3	1.310	1.320	1.331	1.344	1.351	1.370	1.386	1.410	1.442
	1.310	1.326	1.337	1.344	1.347	1.370	1.382	1.406	1.442
S4	1.308	1.316	1.327	1.340	1.356	1.368	1.392	1.415	1.447
	1.312	1.322	1.332	1.340	1.352	1.368	1.388	1.411	1.451
S5	1.315	1.312	1.319	1.335	1.357	1.372	1.393	1.412	1.450
	1.311	1.318	1.330	1.339	1.348	1.363	1.389	1.408	1.450
S6	1.305	1.311	1.326	1.343	1.355	1.373	1.388	1.417	1.457
	1.309	1.317	1.326	1.343	1.346	1.364	1.384	1.408	1.453
EB1	1.313	1.321	1.324	1.341	1.364	1.375	1.387	1.399	1.426
	1.313	1.321	1.324	1.331	1.348	1.360	1.372	1.389	1.433
EB2	1.315	1.322	1.325	1.326	1.336	1.350	1.394	(1.416)	1.444
	1.315	1.322	1.325	1.326	1.336	1.350	1.377	(1.395)	1.439
EB3	1.315	1.319	1.323	1.327	1.327	1.335	1.341	1.370	1.458
	1.314	1.319	1.323	1.327	1.331	1.335	1.341	1.374	1.458
Average of observed ratios	1.317	1.328	1.337	1.348	1.359	1.372	1.388	1.410	1.447

---

[1] The upper row of figures for each fuel is the observed ratio; the lower row, the calculated.

The effect of slope of the A.S.T.M. evaporation curves at the 10, 50, and 90 percent points on the temperatures of 16:1 resultant mixtures is shown in figure 10 for three hypothetical fuels which have identical A.S.T.M. temperatures at these three points. At the 10 percent point, fuel I, with the largest slope, shows a 16:1 temperature 6° C. higher than fuel III with the smallest slope; at the 50 percent point, all three fuels have the same 16:1 temperature regardless of the slope; and at 90 percent, fuel I, with the largest slope, shows a 16:1 temperature 15° C. lower than fuel III, with the smallest slope.

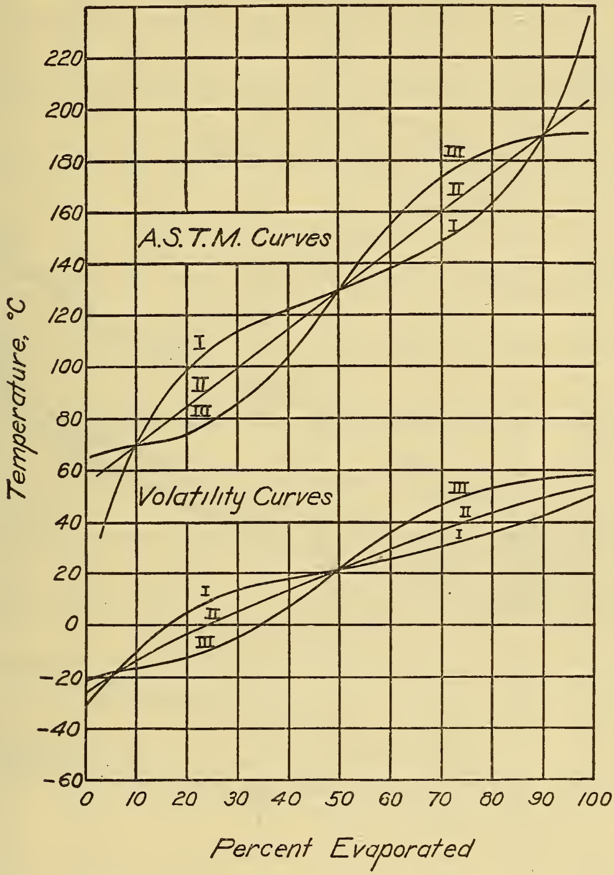


Figure 10.—*Volatility and A.S.T.M. evaporation curves for 3 hypothetical fuels showing the effects of variation in slope of the A.S.T.M. curves at 10, 50, and 90 percent evaporated.*

The types of volatility curves obtained with aviation fuels, benzene blends and ethyl ether blends are shown respectively in figures 11, 12, and 13. In each figure, the upper set of curves are the A.S.T.M. evaporation curves of the fuels, while the lower set are volatility curves representing the temperatures corresponding to 16:1 resultant air-vapor mixtures formed from the above fuels. Descriptions of these fuels, including the composition of the blends, have been given in table 1.

(c) APPLICATION TO DEW-POINT DATA

In the preliminary correlation of the dew points with the A.S.T.M. data, it was found that a relation existed between the dew-point temperatures and the A.S.T.M. evaporation temperatures at 90 percent evaporated. Accordingly, the following relation analogous to equation 28 should hold for dew points.

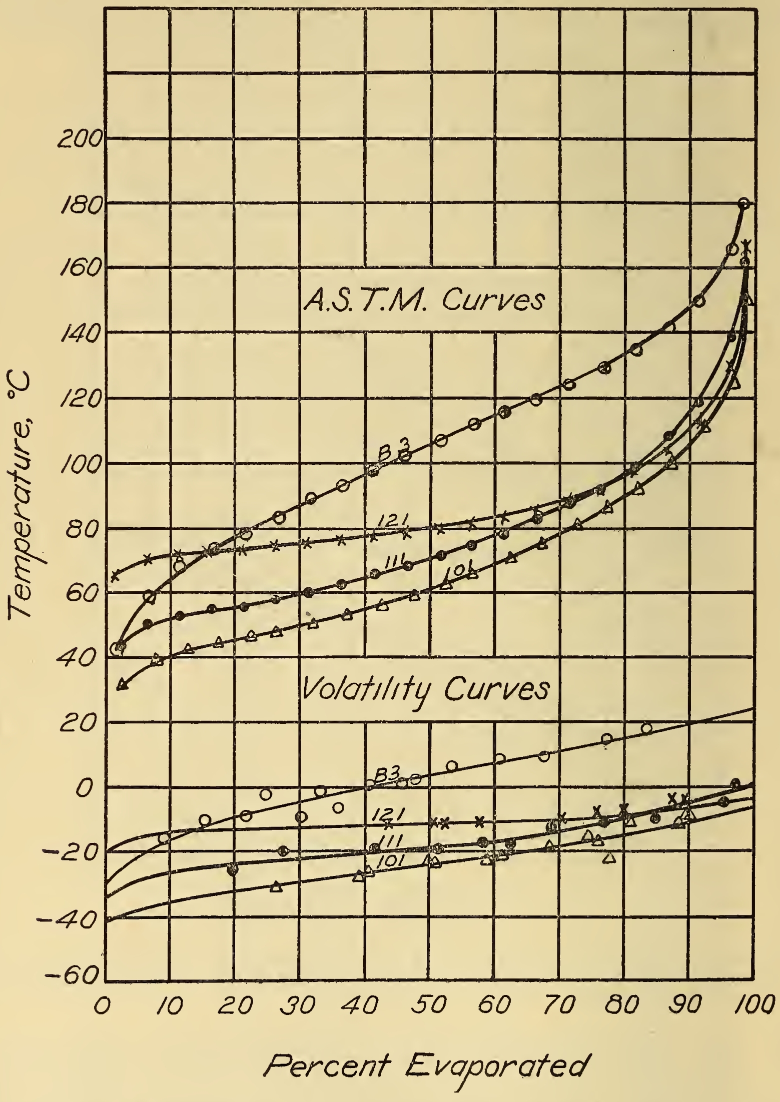


FIGURE 11.—*Volatility and A.S.T.M. evaporation curves for aviation fuels.*

$$\frac{T_{90\%}}{T_{DP16}} = 1.5 - \frac{C}{T_{DP16}} \tag{30}$$

where the temperatures are in absolute centigrade degrees, and C is a function of the slope S of the A.S.T.M. evaporation curve at the 90 percent point, expressed as degrees centigrade change per unit change in the percentage evaporated. The relation between C and the slope S is

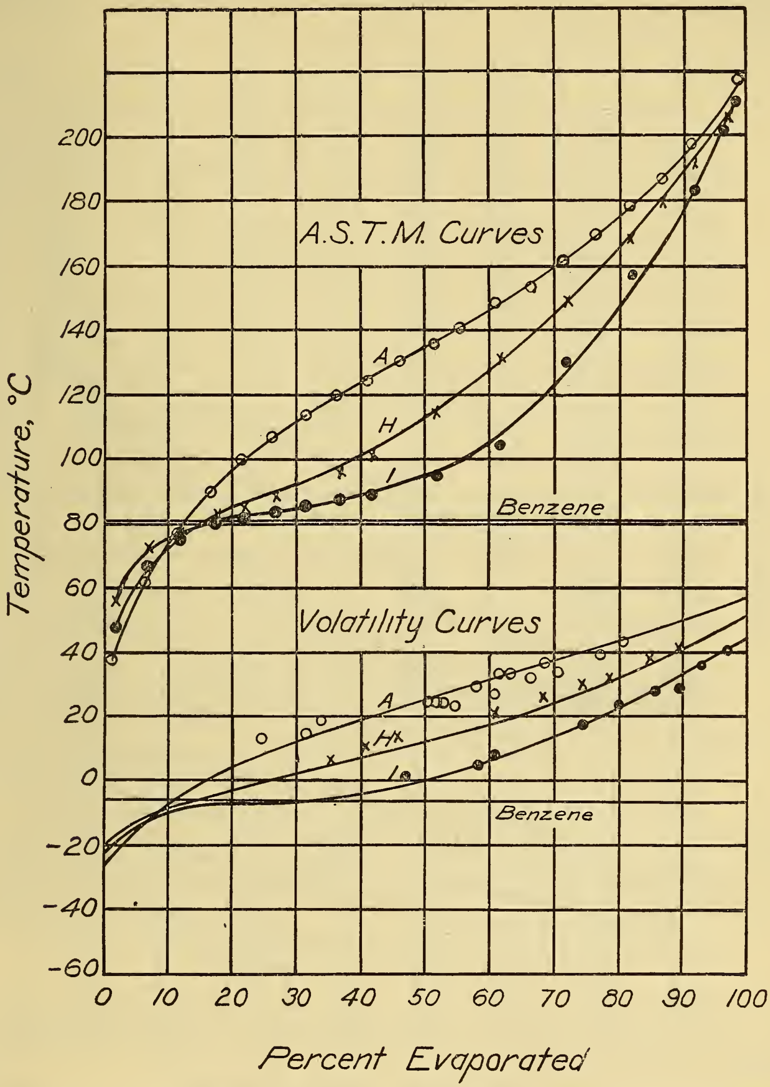


FIGURE 12.—*Volatility and A.S.T.M. evaporation curves for benzene blends.*

$$C = -10\sqrt{S} + 39 \tag{31}$$

Equations 30 and 31 may be combined and rearranged to give

$$1.5\, t_{DP_{16}} = t_{90\%} - 10\sqrt{S} + 39 \tag{32}$$

where the temperatures are in centigrade degrees. These equations are applicable to pure hydrocarbons, conditioned by $S=0$.

For each gasoline, the value of the ratio $T_{90\%}/T_{DP_{16}}$ was computed using equations 30 and 31. These computed ratios are compared in table 12 with the ratios obtained from the experimentally determined dew points. The data for fuels 1A, 2A, 3A, and 4A, are shown in parentheses, because they were obtained by extrapolation over a much longer range than usual.

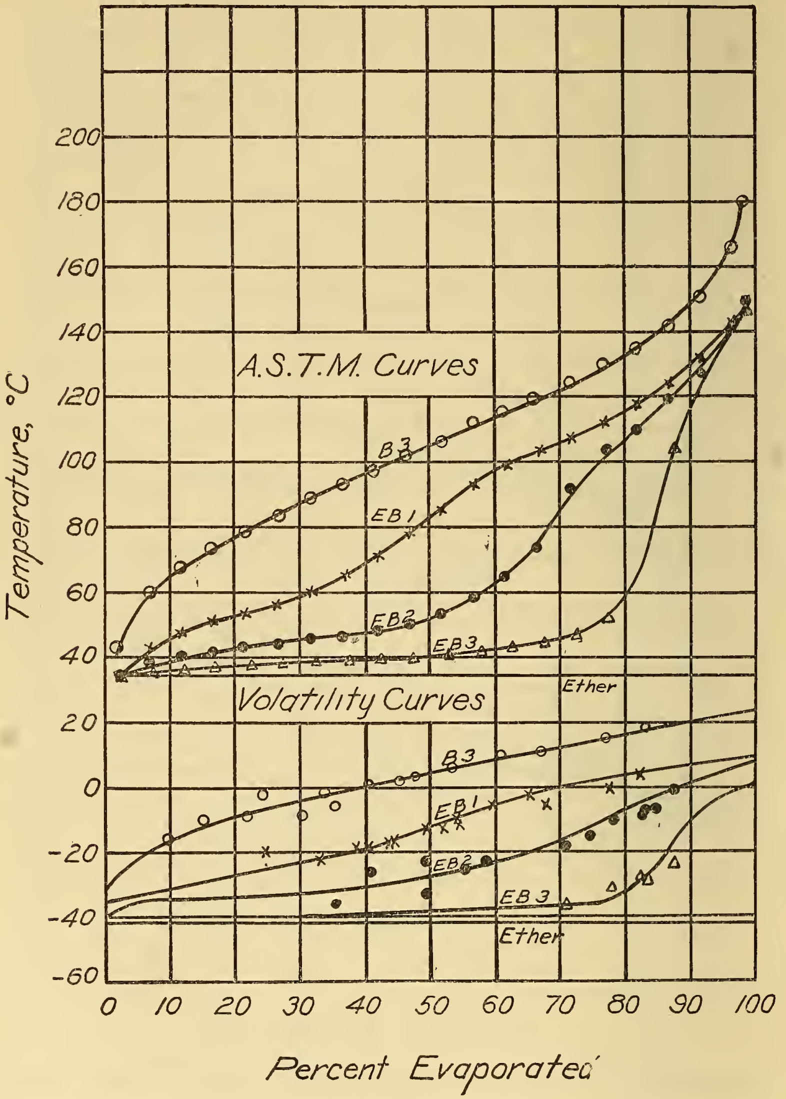


FIGURE 13.—*Volatility and A.S.T.M. evaporation curves for ethyl ether blends.*

TABLE 12.—*Dew-point data for 16:1 mixtures*

Fuel number	90 percent point	Slope	$T_{90\%}/T_{DP_{16}}$ Observed	$T_{90\%}/T_{DP_{16}}$ Calculated	Difference between observed and calculated temperature
					°C
1	199	2.1	1.422	1.426	1
2	195	2.4	1.423	1.427	1
3	197	2.1	1.429	1.425	−1
1A	195	2.8	(1.431)	1.431	0
2A	195	2.7	(1.436)	1.431	−1
3A	193	2.4	(1.430)	1.426	−1
4A	186	2.3	(1.426)	1.426	0
A	196	2.3	1.426	1.426	0
B	132	1.7	1.411	1.406	−1
C	174	3.2	1.428	1.428	0
D	200	5.4	1.434	1.447	3
E	199	2.4	1.426	1.426	0
F	198	2.0	1.428	1.424	−1
RH	168	2.2	1.423	1.419	−1
L	152	1.8	1.417	1.417	0
6	190	2.5	1.420	1.424	1
G	178	3.2	1.423	1.432	2
H	186	2.5	1.421	1.425	1
I	177	3.4	1.420	1.429	2
RPC	198	2.2	1.419	1.423	1
J	207	2.0	1.420	1.424	1
K	176	2.2	1.425	1.421	−1
N	204	1.7	1.415	1.419	1
O	200	1.7	1.408	1.420	3
M	222	3.0	1.423	1.435	3
B3	148	2.0	1.418	1.418	0
101	106	2.5	1.409	1.409	0
111	115	2.5	1.416	1.411	−1
121	110	2.3	1.408	1.408	0
S1	165	1.7	1.422	1.413	−2
S2	166	1.8	1.425	1.416	−2
S3	161	2.0	1.414	1.418	1
S4	161	2.4	1.418	1.423	1
S5	159	2.5	1.421	1.421	0
S6	154	2.8	1.419	1.423	1
EB1	128	1.8	1.417	1.407	−2
EB2	124	2.1	1.413	1.413	0
EB3	112	3.8	1.410	1.420	2
Average observed ratio=1.421 Grand average deviation=					1.0

The effect of slope is illustrated in figure 14 for three hypothetical fuels having the same 90 percent point, slopes varying from 0 to 5.0. The fuel with the greatest slope has a dew point 13° C lower than the fuel with zero slope.

(d) APPLICATION TO BUBBLE-POINT DATA

In accordance with the preliminary relation found between the 16:1 bubble points and the temperatures at 10 percent evaporated on the A.S.T.M. evaporation curves, equation 28 becomes for bubble points:

$$\frac{T_{10\%}}{T_{BP_{16}}}=1.5-\frac{C}{T_{BP_{16}}} \tag{33}$$

where the temperatures are in absolute centigrade degrees. The relation between C and the slope of the A.S.T.M. evaporation curve at the 10 percent point is as follows:

$$C=-10\sqrt{S}+39 \tag{34}$$

It is interesting that equation 34 is formally identical with equation 31, relating C and S at the 90 percent point in the evaluation of dew points.

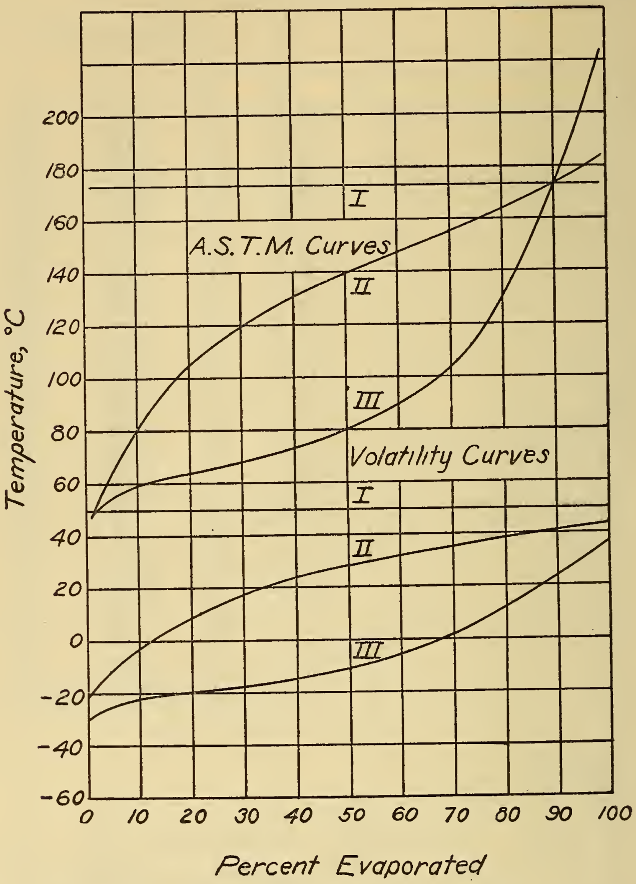


FIGURE 14.—*Volatility and A.S.T.M. evaporation curves for 3 hypothetical fuels showing the effect on the dew point of variation in the slope of the A.S.T.M. curve at 90 percent evaporated.*

The ratio $T_{10\%}/T_{BP_{16}}$ was computed for each fuel by means of equations 33 and 34 and a comparison is made in table 13 between these computed ratios and those obtained from the experimentally determined bubble points.

TABLE 13.—*Bubble-point data for 16:1 mixtures*

Fuel	$T_{10\%}/T_{BP16}$		S	10% point
	Obs.	Comp.		
				° C
A	1.410	1.414	3.0	75
B	1.400	1.400	2.1	63
C	1.401	1.402	2.2	69
J	1.408	1.402	2.5	54
M	1.409	1.410	2.5	89

Average observed ratio = 1.406.

The effect of slope at the 10 percent point is illustrated in figure 15 for three hypothetical fuels having the same 10 percent point, but

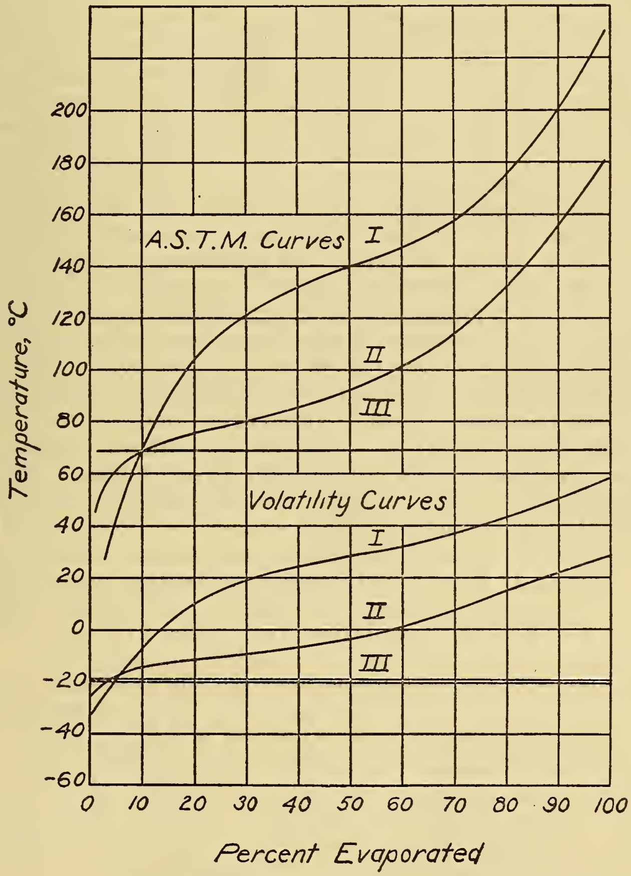


FIGURE 15.—*Volatility and A.S.T.M. evaporation curves for 3 hypothetical fuels showing the effect on the bubble point of variation in slope of the A.S.T.M. curve at 10 percent evaporated.*

slopes varying from 0 to 5.0. The fuel with the greatest slope has a bubble point 14° C lower than the pure hydrocarbon with zero slope.

VIII. ACCURACY OF VOLATILITY DATA AND OF CORRELATION WITH A.S.T.M. DISTILLATION DATA

1. CONSIDERATION OF PARTIAL VOLATILITY

The accuracy of the partial volatility data is largely determined by the precision of calibration of the equilibrium air-evaporation apparatus and accessories and by the sensitivity of the method. The estimated precisions of the various parts of the apparatus and of the factors affecting the accuracy of the results, based on the calibration data and on experimental checks, are as follows:

Air feed	0. 2 percent
Gasoline feed	0. 2 percent
Volume of residue	0. 2 percent
Specific gravity determinations	0. 1 percent
Evaporation bath temperature	0. 1 C
Time for collection of residue	0. 3 percent

Considering the various factors involved, it is estimated that the observed data are precise to 1 unit in the percentage evaporated. The correction for the departure from equilibrium vaporization was found to be precise likewise to 1 unit in the percentage evaporated, so that individual results, corrected to equilibrium, may be considered precise to 2 units in the percentage evaporated. The method used of drawing smooth curves through the plotted experimental points tends to minimize the experimental errors, so that a precision of 2 units in the percentage evaporated for the equilibrium air-evaporation apparatus appears to be a liberal estimate. At percentages evaporated around 95 percent or above, where the volume of residue collected is small, errors in excess of 2 units may be obtained, but in general the slope of the volatility curves is such that the corresponding errors in the temperature are small. At very small percentages evaporated, the slope of the supplied air-fuel mixture curves is large and a small error in the percentage evaporated causes a large corresponding error in the temperature on the resultant air-vapor curve. Below 5 percent evaporated, the precision of the equilibrium air-evaporation apparatus is very unsatisfactory. Over the range from 10 to 90 percent evaporated an error of 2 units in the percentage evaporated produces on the average an error of 1° C in the temperatures on the resultant air-vapor curves. Hence, 1° C may be taken as the average error in the partial volatility data. Using the precautions, previously outlined, in making the A.S.T.M. distillation tests, the average error in the temperatures on the A.S.T.M. evaporation curves is 1° C.

The accuracy of the correlation between the observed temperatures on the 16:1 air-vapor curves for the 38 fuels and those computed by means of equations 28 and 29 from the A.S.T.M. distillation data can be observed from the temperature ratios listed in table 11. The distribution of temperature deviations between the observed and calculated values is given in table 14. About 87 percent of the points show deviations less than 2° C. Of the three points which showed deviations greater than 3° C, two amounted to 4° C and the other to 7° C. It is believed that the deviations at these three points are without significance, being attributable to experimental error, and for this reason the ratios at these three points are shown in parentheses in table 11. For further comparison, the temperature deviations between the observed and computed 16:1 temperatures are shown graphically in figures 16, 17, and 18 for 10, 50, and 90 percent evap-

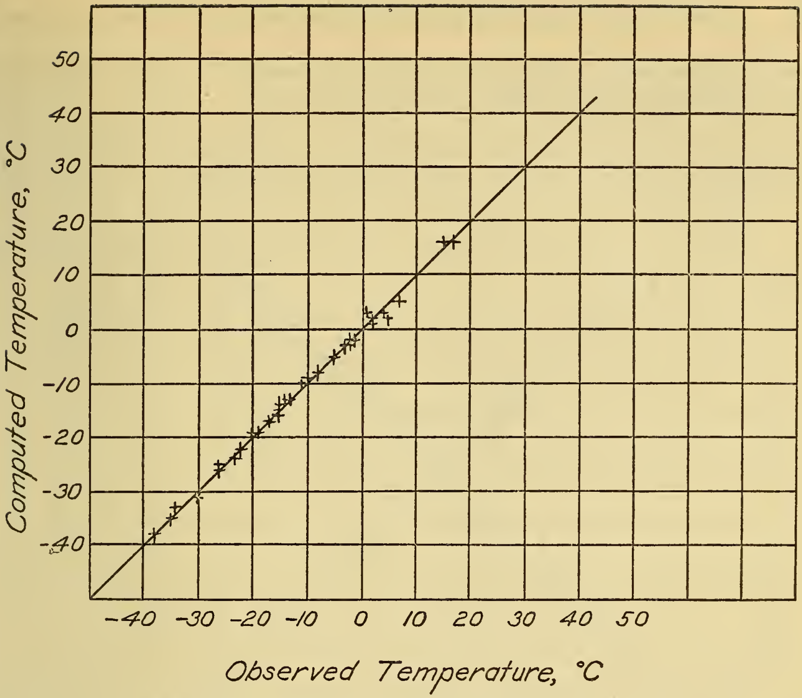


FIGURE 16.—*Plot showing agreement between observed and computed volatility data at 10 percent evaporated.*

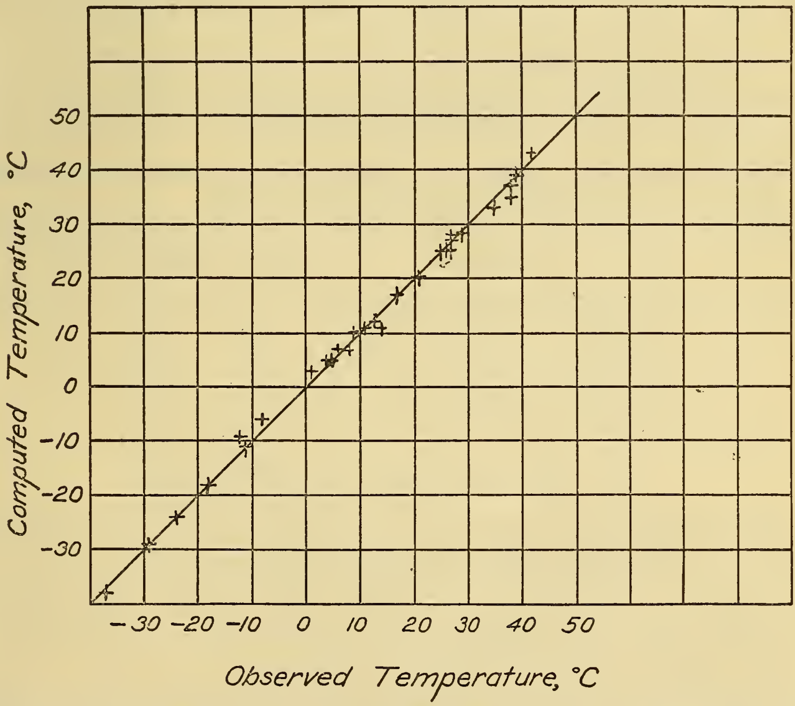


FIGURE 17.—*Plot showing agreement between observed and computed volatility data at 50 percent evaporated.*

orated respectively. The grand average deviation between observed and computed values for the 38 fuels is 1° C.

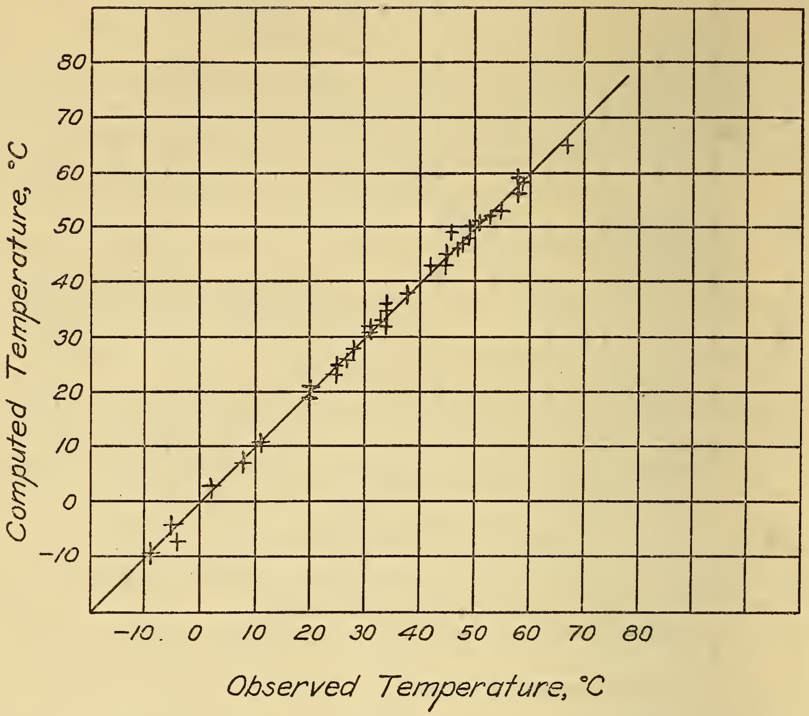


FIGURE 18.—*Plot showing agreement between observed and computed volatility data at 90 percent evaporated.*

TABLE 14.—*Distribution of temperature deviations between observed and computed values from 10 to 90 percent inclusive.*

Deviation ° C	Number of points	Percent of points
Above 3	3	0.9
3	22	6.4
2	50	14.6
1	150	43.9
0	117	34.2

Grand average deviation=1° C.

2. CONSIDERATION OF DEW POINTS

The dew-point data are subject to somewhat greater error than the partial volatility data since they are obtained by extrapolation of the latter over a range of about 5 percent, on the average, to the line of 100 percent evaporated. Considering the accuracy of the partial volatility data, it is estimated that the dew points obtained by the extrapolation process are accurate to 2° C.

The accuracy of the correlation between the dew points and the 90-percent A.S.T.M. points is illustrated in the last column of table

12 which lists the temperature differences between the observed and computed values. The distribution of temperature deviations is given in table 15. About 74 percent of the points show deviations less than 2° C., and only 3 out of the 34 fuels show deviations amounting to 3° C. For further comparison, the temperature deviations between the observed and computed 16:1 dew points are shown graphically in figure 19.

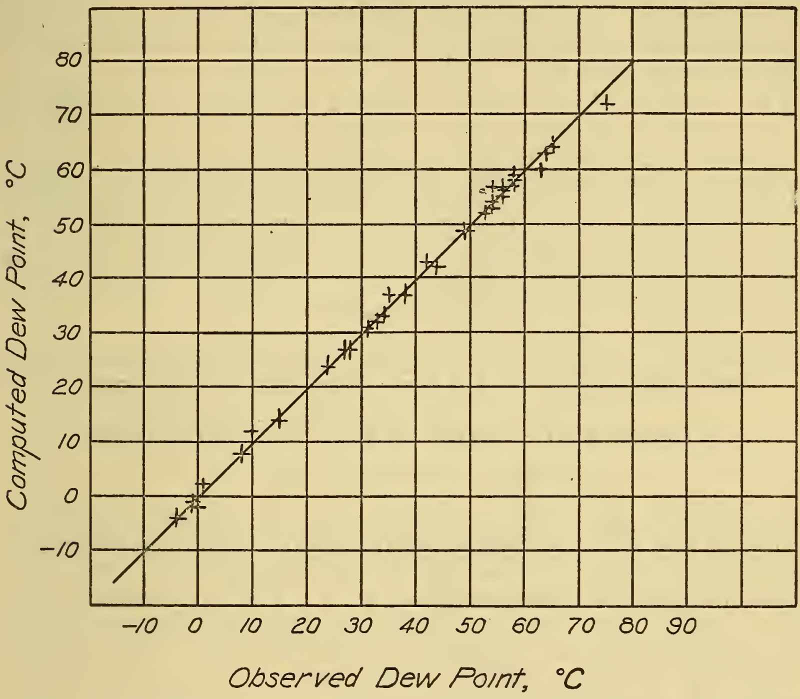


FIGURE 19.—*Plot showing agreement between observed and computed dew points.*

TABLE 15.—*Distribution of temperature deviations between observed and computed dew-point values.*

Deviation ° C	Number of points	Percent of points
3	3	8.8
2	6	17.6
1	16	47.1
0	9	26.5

3. CONSIDERATION OF BUBBLE POINTS

The accuracy of the bubble-point data depends upon the accuracy of the molecular weight values for the gasoline vapors present in the small bubbles, upon the accuracy of the vapor-pressure values for the gas-free gasolines, and upon how closely the gasoline vapors obey the perfect gas laws at the low pressures under consideration.

The indirect evaluation of the molecular weights of the vapors has an estimated accuracy of 5 units in molecular weight. Considering the probable deviations from the perfect gas laws, the corresponding error in the vapor pressure of the gasoline amounts to 2 mm of mercury. This is also the accuracy of the experimentally determined vapor pressures over a range of temperatures. Since a change of 1° C produces a corresponding change of 1 mm in the vapor pressure under the conditions considered, it is estimated that the bubble points are accurate to about 2° C.

In the correlation of the 16:1 bubble point temperatures with the A.S.T.M. 10-percent points, the average deviation between the observed and computed temperature ratios, as given in table 13, amounts to 0.0024. This is equivalent to an average temperature deviation of less than 1° C. However, since 5 gasolines only were studied, these data alone are hardly sufficient to verify the generality of the relations. Further verification of an indirect nature has been obtained in another investigation from extensive vapor pressure measurements on a large number of gasolines.

IX. DETAILED METHOD FOR EVALUATION OF VOLATILITY DATA FROM A.S.T.M. DISTILLATION DATA

1. COMPUTATION FROM VOLATILITY EQUATIONS

(a) PARTIAL VOLATILITY DATA

The first step in obtaining volatility data on a gasoline consists in making an A.S.T.M. distillation, preferably observing the precautions regarding temperature control pointed out in section IV. These distillation data are then used to obtain an A.S.T.M. evaporation curve, which is simply the customary distillation curve displaced to the right by an amount equal to the observed distillation loss. If it is desired to obtain the complete volatility curve for a 16:1 resultant mixture, the slope of the A.S.T.M. evaporation curve at every 10 percent evaporated is evaluated, by either of two methods. One of these is to employ the customary graphical method of laying a straight edge tangent to the curve at the point under consideration and reading the temperature difference along the line thus formed for a change of 10 percent in the percentage evaporated. The temperature difference, in degrees centigrade, divided by 10 is the desired slope. A second, less accurate method consists in reading the temperatures on the curve at 5 percent more and 5 percent less than the percentage evaporated under consideration, in subtracting the latter from the former, and finally dividing by 10. The second method ordinarily gives sufficient accuracy for the purpose if there is not a very marked change in curvature in the 10 percent range considered. For example, it is desired to find the slope of an A.S.T.M. evaporation curve at 40 percent evaporated. The temperature at 45 percent evaporated is found to be 130 C and at 35 percent evaporated, it is 110 C. Subtracting 110 from 130 gives 20, which when divided by 10 gives 2 as the slope at 40 percent evaporated.

The values of the slope at every 10 percent evaporated are then used to compute values of the parameter C at each value of the percentage evaporated P by means of equation 29.

$$C=\sqrt{460S}\cdot\log_{10}\left[\frac{100-P}{50}\right]+39 \qquad (29)$$

The next step is to read the temperatures on the plotted A.S.T.M. evaporation curve of the gasoline at every 10 percent evaporated from 10 to 90 percent. These temperatures together with the corresponding values of C, obtained from equation 29, at the same percentages evaporated, are used to compute the 16:1 temperatures by means of equation 28. In order to simplify the calculation, equation 28 may be written as follows:

$$1.5t_{16}=t_{\text{ASTM}}-(136.6-C) \qquad (34)$$

where t_{16} and t_{ASTM} are in centigrade degrees. The value of C at the percentage evaporated under consideration is subtracted from 136.6 and the resulting number is subtracted from the temperature on the A.S.T.M. evaporation curve at the same percentage evaporated as was used for the evaluation of C. This difference divided by 1.5 gives the 16:1 temperature at the particular percentage evaporated. Similar computations are made for the values at every 10 percent evaporated from 10 to 90 percent. It should be emphasized that the values of S, C, t_{ASTM} and t_{16} always refer to a common percentage evaporated when computing partial volatility data.

Example: A gasoline has an A.S.T.M. evaporation temperature of 100 C at 30 percent evaporated and has a slope of 2.0 at 30 percent evaporated. It is desired to know the temperature at which a mixture of 16 parts of air and 1 part of vapor from this gasoline will form at 30 percent evaporated. Equation 29 gives 43.4 as the value of C at 30 percent evaporated. Substituting in equation 34 the above value of C and 100 for t_{ASTM}, the 16:1 temperature at 30 percent evaporated is found to be 4.5 C.

(b) DEW-POINT DATA

The first step in obtaining dew point data on a gasoline consists in determining the value of the slope of the A.S.T.M. evaporation curve at 90 percent evaporated. From this value of the slope, C is computed by means of equation 31

$$C=-10\sqrt{S}+39 \qquad (31)$$

The next step consists in reading the temperature on the A.S.T.M. evaporation curve at 90 percent evaporated. This temperature together with the value of C from equation 31 is used to obtain the 16:1 dew point by means of equation 30, which may be written in the simpler form

$$1.5t_{DP16}=t_{90\%}-(136.6-C) \qquad (35)$$

where t_{DP16} and $t_{90\%}$ are in centigrade degrees.

When computing dew point data, S and $t_{90\%}$ refer to 90 percent evaporated whereas C and t_{DP16} refer to 100 percent evaporated.

Example: A gasoline has an A.S.T.M. evaporation temperature of 200 C at 90 percent evaporated and the A.S.T.M. evaporation curve has a slope of 2.0 at 90 percent evaporated. It is desired to know the dew point of a 16:1 mixture of air and this gasoline. From equation 31, C is found to have a value of 24.9. Substituting this value of C

in equation 35 together with 200 for $t_{90\%}$ and dividing the resultant summation by 1.5 gives 58.9 C. This is the desired 16:1 dew point.

(c) BUBBLE-POINT DATA

The first step in obtaining bubble-point data on a gasoline consists in determining the slope of the A.S.T.M. evaporation curve at 10 percent evaporated. From this value of the slope, C is computed by means of equation 33

$$C = -10\sqrt{S} + 39 \tag{33}$$

The next step consists in reading the temperature on the A.S.T.M. evaporation curve at 10 percent evaporated. This temperature together with the value of C from equation 33 is used to obtain the 16:1 bubble point by means of equation 32, which may be written:

$$1.5t_{BP16} = t_{10\%} - (136.6 - C) \tag{36}$$

where t_{BP16} and $t_{10\%}$ are in centigrade degrees.

When computing bubble-point data, S and $t_{10\%}$ refer to 10 percent evaporated, whereas C and t_{BP16} refer to 0 percent evaporated.

Example: A gasoline has an A.S.T.M. evaporation temperature of 60 C at 10 percent evaporated and the A.S.T.M. evaporation curve has a slope of 2.0 at 10 percent evaporated. It is desired to know the bubble point of a 16:1 mixture of air and this gasoline. From equation 33, C is found to have a value of 24.9. Substituting this value of C in equation 36 together with 60 for $t_{10\%}$, the desired bubble point $t_{BP_{16}}$ is -34.5 C.

(d) VOLATILITY DATA AT OTHER PERCENTAGES EVAPORATED AND FOR OTHER MIXTURES

Having the 16:1 temperatures at every 10 percent evaporated from 0 to 100 percent, the value at any intermediate percentage evaporated may be obtained by plotting the computed temperatures against the corresponding percentages evaporated, by drawing a smooth curve through the plotted points and by reading off this curve the temperatures at the desired percentages evaporated.

From the 16:1 values, the temperatures may readily be obtained corresponding to the formation, under equilibrium conditions, of any other desired mixture of air and gasoline vapor from 8:1 to 20:1. A method for making such transformations was indicated in figure 7, where the differences in temperature found between the various resultant mixture lines were shown as a curve. The equation of this curve can be written as follows:

$$t_{M_R} - t_{16} = 52.5 - 43.5 \log_{10} M_R \tag{37}$$

where M_R is the resultant air-vapor mixture and t_{M_R} is the temperature in centigrade degrees corresponding to the formation of the mixture M_R. In this equation, t_{M_R} and t_{16} refer to the same percentage evaporated, but the difference $t_{M_R} - t_{16}$ is the same at all percentages evaporated, being only dependent within experimental error on the value of M_R. Hence having the value of t_{16}, the temperature for any other mixture within the limits stated, may be computed.

Example: A gasoline has a 16:1 temperature of 4.5 C at 30 percent evaporated. It is desired to know the temperature corresponding to the formation of an 8:1 mixture at 30 percent evaporated. Substituting 8 for M_R in equation 37, $t_8 - t_{16}$ equals 13.1. Adding 13.1 to 4.5 gives 17.6 C which is the desired 8:1 temperature.

While equation 37 holds with sufficient accuracy for all of the gasolines studied, the difference between any two resultant mixture lines does depend to a slight extent upon the volatility of the gasoline. A more precise equation is as follows:

$$t_{M_R} - t_{16} = [0.132 - 0.109 \log_{10} M_R](t_{\text{ASTM}} + 273) \tag{38}$$

Equation 38 reduces to equation 37 for a value of t_{ASTM} equal to 125 C.

2. GRAPHICAL EVALUATION OF VOLATILITY DATA

The detailed computation of partial volatility, dew-point and bubble-point data on gasolines from the A.S.T.M. distillation data may be avoided by the use of charts. Equations 29, 31, and 33 for the evaluation of the parameter C may be combined in one alinement chart. Equations 34, 35, and 36 may be combined in another alinement chart to give directly the temperatures corresponding to the formation of 16:1 resultant air-vapor mixtures. A duplex scale, based on equation 37, can be used to indicate the differences in temperature between 16:1 mixture lines and other mixture lines of interest. Accordingly, two alinement charts and a duplex scale have been designed so that they are as accurate as is justified from the experimental work on which they are based, namely, 1° C.

(a) CHART FOR EVALUATION OF PARAMETER C

The alinement chart for the evaluation of C from the slope of the A.S.T.M. evaporation curve and the percentage evaporated is shown in figure 20. The scale on the left, marked P, represents percentages evaporated. The horizontal scale, marked S, represents the slope of the A.S.T.M. evaporation curve. The scale on the right, marked C, represents values of the parameter C. The identical points, marked D.P. and B.P., on the P scale slightly above 80 percent evaporated are for the evaluation of C in connection with dew points and bubble points.

In using the chart, connect by means of a straight edge the appropriate mark on the P scale with the corresponding value of the slope of the A.S.T.M. evaporation curve on the S scale. The intersection of this line with the C scale gives the desired value of C. Three precautions should be observed in using this chart:

(1) In evaluating C for partial volatility data, the value of S refers to the percentage evaporated P under consideration.

(2) For dew point data, S refers to the slope at 90 percent evaporated.

(3) For bubble point data, S refers to the slope at 10 percent evaporated.

Solutions for a number of cases are given below:

P scale	S scale	Intersection on C scale
10	2.0	47
50	Any value	39
Any value	0.0	39
90	2.0	18
D.P.	2.0	25
B.P.	1.0	29

It is to be noted that when $P=50$, the slope of the A.S.T.M. evaporation curve has no effect and $C=39$ in all cases. Further, when $S=0$, C has the same value, namely, 39, at all percentages evaporated.

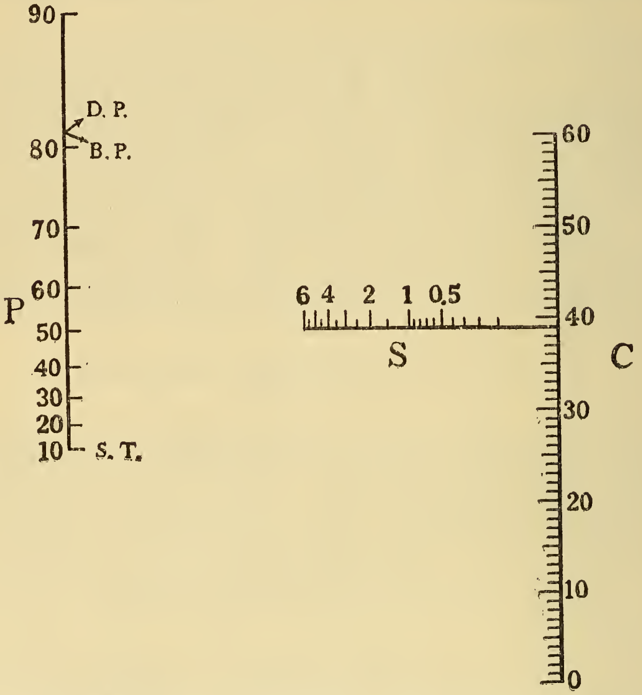
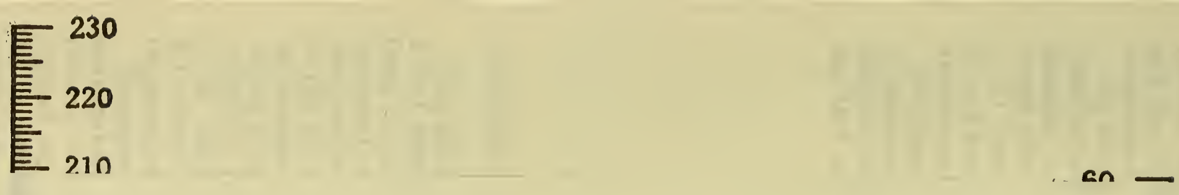


FIGURE 20.—*Alinement chart for evaluation of the parameter C in equations 29, 31, and 33 from the percentage evaporated P and the slope S of the A.S.T.M. evaporation-curve.*

(b) CHART FOR EVALUATION OF 16:1 TEMPERATURES

The chart for the evaluation of the temperatures on a 16:1 resultant air-vapor line from the values of C and the A.S.T.M. evaporation temperature is shown in figure 21. The scale on the left represents A.S.T.M. evaporation temperatures in centigrade degrees; the middle scale represents values of the parameter C; whereas the scale on the right represents temperatures in centigrade degrees for a 16:1 resultant mixture of air and gasoline vapor.

In using the chart, connect by means of a straight edge the appropriate mark on the A.S.T.M. temperature scale with the correspond-


230
220
210
60

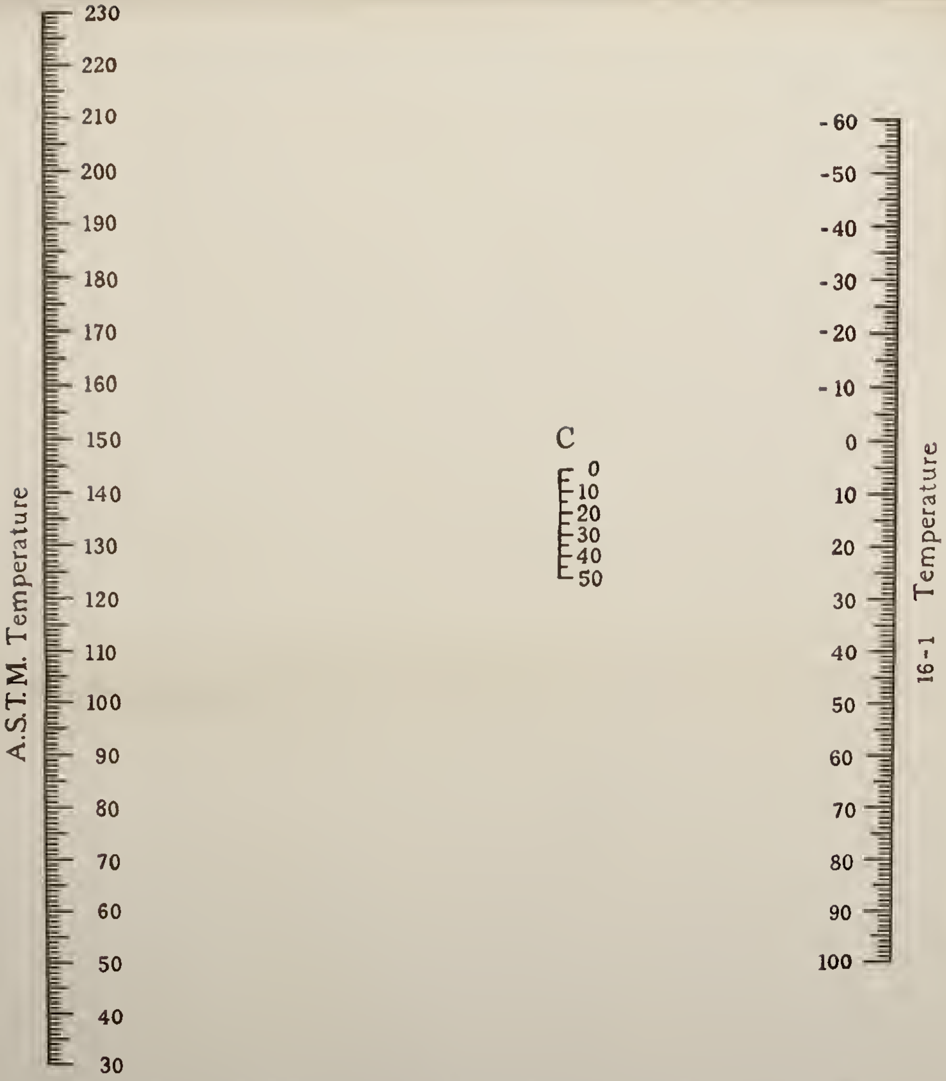


FIGURE 21.—*Alinement chart for evaluation of 16:1 temperatures on the volatility curve from the temperature on the A.S.T.M. evaporation curve and the value of the parameter C obtained from figure 20.*

ing value of C on the middle scale, and extrapolate the line thus formed to cut the 16:1 temperature scale. The intersection of the line with the scale gives the desired 16:1 temperature. The precautions which should be observed in using this chart are as follows:

(1) In the evaluation of partial volatility data, the A.S.T.M. temperature and the value of C refer to the same percentage evaporated, and the 16:1 temperature found applies also to this same percentage evaporated.

(2) For dew-point data, the 90 percent A.S.T.M. evaporation temperature is used together with the value of C obtained in the special manner outlined in the last subsection, and the 16:1 temperature found refers to 100 percent evaporated.

(3) For bubble-point data, the 10 percent A.S.T.M. temperature is used together with the value of C appropriate to bubble point evaluations and the 16:1 temperature found refers to 0 percent evaporated.

Solutions for a number of cases are given below. The first column of percentages evaporated P refers to the A.S.T.M. evaporation curve. The last column, marked P, refers to the percentages evaporated on the 16:1 air-vapor line.

A.S.T.M. evaporation data		16:1 volatility data		
P	Temperature	C	Temperature	P
	°C		°C	
10	60	29	−32	0
10	60	47	−20	10
50	125	39	18	50
90	180	18	41	90
90	180	25	46	100

(c) DUPLEX SCALE FOR TEMPERATURE DIFFERENCES BETWEEN RESULTANT MIXTURE LINES

The duplex scale for obtaining the difference in temperature between a 16:1 resultant air-vapor mixture line and other resultant mixture lines is shown in figure 22. The marks on the left of this scale represent resultant mixtures M_R and those at the right represent the temperature differences ΔT which are to be added algebraically to the 16:1 temperatures. These differences are independent of the percentage evaporated and the volatility of the particular gasoline, within experimental error. Thus the scale may be used for partial volatility, dew point and bubble point data. The only condition to be observed is that the temperature obtained after addition of ΔT refers to the same percentage evaporated as the original 16:1 temperature.

Example: The temperature on a 16:1 mixture line at 90 percent evaporated is 40 C. It is desired to know the temperature at 90 percent evaporated corresponding to the formation of a 20:1 mixture of air and vapor from this gasoline. From the duplex scale, ΔT is found to be -4 for $M_R=20$. Adding -4 to 40 gives 36 C, which is the desired temperature.

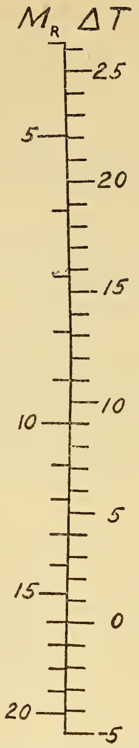


FIGURE 22.—*Duplex scale showing temperature differences between volatility curves for various resultant air-vapor mixtures*

3. SPECIAL CHART FOR DEW-POINT DATA

Although the charts shown in figures 20 and 21 are satisfactory for the evaluation of dew points, a more convenient graphical method for such data is illustrated in figure 23.

Duplex scale I gives the dew points directly for a gasoline having a slope of 2.0 at 90 percent evaporated on the A.S.T.M. evaporation curve, which represents an average value. The temperatures in centigrade degrees at 90 percent evaporated are placed on the left side of this scale whereas the corresponding dew points, in centigrade degrees, for a 16:1 mixture are placed on the right side of the scale. Duplex scale II indicates the temperature correction for the 16:1 dew point of the gasoline if it has a slope other than 2.0 at 90 percent evaporated. The marks on the left side of scale II represent slopes at 90 percent evaporated, whereas those on the right represent corrections which are to be added algebraically to the dew-point values from scale I.

Example: A gasoline has a temperature of 150 C at 90 percent evaporated and a slope of 4.0 at this point on the A.S.T.M. evaporation curve. It is desired to know the 16:1 dew point of this gasoline. From scale I, a 90 percent point of 150 C corresponds to a 16:1 dew point of 25 C. From scale II, a slope of 4.0 indicates a correction of plus 4. Therefore the desired dew point is 29 C.

4. COMPLETE EXAMPLE OF EVALUATION OF VOLATILITY DATA

A further illustration of the method of obtaining volatility data from distillation data is outlined in detail below. The distillation data on a gasoline are given in table 16. These data are plotted in the form of an evaporation curve as explained previously. At every 10 percent evaporated from 10 to 90 percent evaporated, the temperatures are read off the evaporation curve and are listed in the second column of table 17 opposite the appropriate values of the percentage evaporated. The slopes of the A.S.T.M. evaporation curve at these even percentages are obtained in the manner previously outlined and are given in the third column of the table. The fourth column represents the values of C read from figure 20, using the corresponding values of S in the third column and of P in the first column. The fifth column shows the temperatures in centigrade degrees for the 16:1 resultant air-vapor mixture, obtained from figure 21, using the A.S.T.M. evaporation data in the second column and the values of C in the fourth column. The last column lists the temperatures corresponding to an 8:1 resultant air-vapor mixture. The difference in temperature between the last two columns of figures is obtained from the duplex scale in figure 22.

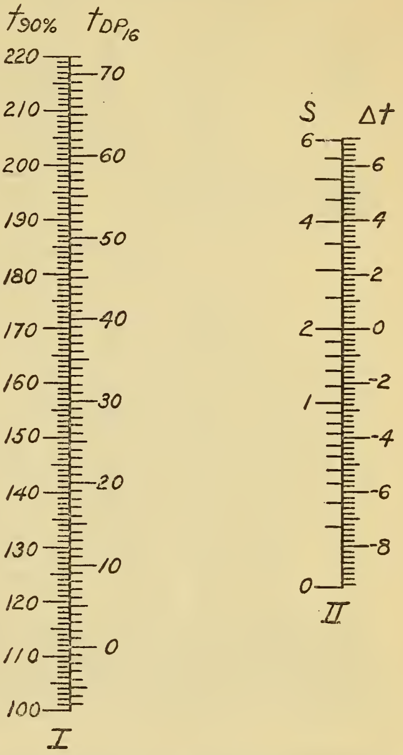


FIGURE 23.—*Duplex scales for evaluation of dew-point values from the temperature at 90 percent evaporated on the A.S.T.M. evaporation curve and from the slope of the evaporation curve at this percent evaporated.*

TABLE 16.—*Distillation data on fuel RPC*

Percent distilled	Temperature	Percent distilled	Temperature	Percent distilled	Temperature
	°*C*		°*C*		°*C*
I.B.P.	38	35	113	70	163
5	57	40	121	75	172
10	69	45	128	80	181
15	79	50	135	85	190
20	88	55	142	90	200
25	97	60	148	95	212
30	105	65	156	E.P.	222

Distillation loss=1.0 percent.
Residue=1.5 percent.

TABLE 17.—*Volatility data for fuel RPC*

Percent evaporated	Temperature	Slope	Value of *C*	16:1 temperature	8:1 temperature
	°*C*			°*C*	°*C*
0	------	------	24	−31	−18
10	66	2.3	47	−15	−2
20	86	1.8	45	−3	10
30	104	1.7	43	9	22
40	119	1.5	41	18	31
50	134	1.3	39	25	38
60	147	1.4	37	32	45
70	162	1.6	33	39	52
80	180	1.8	28	47	60
90	198	2.2	17	52	65
100	------	------	25	58	71

If desired, the 16:1 temperatures may be plotted against the corresponding percentages evaporated and a smooth curve drawn through the plotted points. From this curve the 16:1 temperatures may be obtained at any value of the percentage evaporated.

X. VOLATILITY DATA AT A TOTAL PRESSURE LOWER THAN STANDARD ATMOSPHERIC PRESSURE

The general volatility equations given in preceding sections and all of the experimental volatility data which are presented in this paper are applicable to conditions where the total pressure of the air-vapor mixture is 1 standard atmosphere. In an engine manifold, however, the pressure is normally below 760 mm and may become as low as half an atmosphere in an automobile engine manifold under idling conditions. In the manifold of an unsupercharged airplane engine at high altitudes the pressure may even be below half an atmosphere. In order to make possible the application of volatility data to vaporization in an ideal engine manifold under such conditions of reduced pressure it is desirable to know the temperatures of formation of various resultant air-vapor mixtures at any total pressure below that of the standard atmosphere, 760 mm of mercury.

Although no volatility data have been obtained at pressures other than 760 mm, it is possible to compute similar data at any reduced pressure with sufficient accuracy from the normal atmospheric values.

Consider first the problem of finding the air-vapor mixture M_R' which will be formed at any reduced total pressure p, any percentage

evaporated P, and at the temperature t, which corresponds to an air-vapor mixture M_R, at the same percentage evaporated and at a total pressure of 1 atmosphere. The relation between the mixture ratio and the total pressure is given by equation 23.
Rearranging equation 23, it becomes

$$\frac{760-p_F}{p_F}=M_R\cdot\frac{M_F}{M_A} \tag{39}$$

The analogous relation for any total pressure p is

$$\frac{p-p_F}{p_F}=M_R'\cdot\frac{M_F}{M_A} \tag{40}$$

Dividing equation 40 by equation 39, there results

$$\frac{M_R'}{M_R}=\frac{p-p_F}{760-p_F} \tag{41}$$

The desired air-vapor mixture M_R' can be computed from this relation at any reduced total pressure p if the vapor pressure p_F of the gasoline is known under the stated conditions of temperature and percentage evaporated. In general p_F is, however, not known, but an approximate value can be assumed without introducing much error. For example, for values of M_R from 8 to 20, p_F lies within the limits 5 to 50 mm of mercury for any percentage evaporated. Taking $p_F=5$ mm, $p=380$ mm and $M_R=16$, the value of M_R' from equation 41 is 7.95. For $p_F=50$ mm, $p=380$ mm and $M_R=16$, M_R' becomes 7.45. The difference in temperature between these two mixtures is only 1° C which is negligible in this case, and also for any value of M_R from 8 to 20, as long as the total pressure is not much lower than 380 mm.

Assuming an average value $p_F=30$ and limiting M_R to the range from 8 to 20, equation 41 can be written

$$M_R'=M_R\left[1.04\frac{p}{760}-0.04\right] \tag{42}$$

Suppose a gasoline forms a 16:1 resultant air-vapor mixture at 30 C when 50 percent is evaporated under a total pressure of 760 mm. Then at 30 C and 50 percent evaporated under a total pressure of 380 mm, M_R' is found from equation 42 to equal 7.7, which is the air-vapor mixture formed at this lower pressure.

It should be pointed out that the resultant mixture M_R' given by equation 41 is dependent to a slight extent upon the percentage evaporated, since the vapor pressure p_F changes somewhat with the percentage evaporated along a constant air-vapor mixture line M_R. However, the variations in p_F are within the limits of 5 to 50 mm stated above, and hence for all practical purposes the computed value of M_R' from equation 42 may be considered as independent of the percentage evaporated.

The first problem considered was to find the air-vapor mixture formed at reduced pressure under otherwise similar conditions of temperature and percentage evaporated to those at which a known air-vapor mixture was formed at atmospheric pressure. The second problem is to find the temperature at which a given air-vapor mixture will be formed at any reduced pressure when the temperature is known at which the same air-vapor mixture is formed at atmospheric pressure. This can be easily solved by means of equation 42 supplemented by figure 7 or the duplex scale in figure 22.

Suppose a 16:1 resultant air-vapor mixture is formed at 30 C when 50 percent of a gasoline is evaporated in air at a total pressure of 1 atmosphere. Then at 380 mm total pressure when 50 percent of the gasoline is evaporated M_R is found from equation 42 to be 33.3. This is the mixture formed at 760 mm corresponding to a 16:1 mixture at 380 mm at the same temperature and percentage evaporated. From the curve in figure 7, it is found that a 33.3:1 mixture is formed at a temperature 13° C lower than a 16:1 mixture. Hence, a 16:1 mixture at 380 mm total pressure and at 50 percent evaporated will be formed at $(30-13)=17$ C.

The effect of reduction in total pressure is to enrich the air-vapor mixture formed when the same percentage is evaporated at the same temperature from the same supplied air-fuel mixture. Reduction in pressure under these conditions to one-half an atmosphere makes the mixture approximately twice as rich. In order to obtain the same air-vapor mixture at reduced pressure from the same supplied mixture, when the same percentage is evaporated as at atmospheric pressure, a lower temperature is required. The temperature difference in the two cases is constant for different gasolines and independent of the percentage evaporated. It is also independent of the particular mixture considered, within a range of M_R from 8 to 20, but is dependent upon the reduction in pressure. If a set of volatility curves have been obtained from the distillation data which are applicable to 760 mm total pressure, it is only necessary to lower all of them by a constant temperature difference of 13° C in order that they may be applicable to a total pressure of 380 mm. For application to other pressures, the temperature differences may be computed in the manner outlined or they may be obtained from table 18, by interpolation, if necessary.

TABLE 18.—*Temperature differences between the same resultant mixture curves at 760 mm pressure and at lower pressures*

p, mm mercury	$t_{760}-t_p$	p, mm mercury	$t_{760}-t_p$
	° C		° C
760	0	500	8.1
700	1.5	400	12.6
600	4.5	300	18.6

XI. CONCLUSIONS

The large volume of volatility data which have been obtained on 38 fuels of widely differing characteristics has indicated certain basic principles of fuel volatility. The correlation of the results with the A.S.T.M. distillation data has not only furnished an interpretation of the significance of the distillation data but has also furnished a simple means for the evaluation of equilibrium volatility values from gasoline distillation data. While the information obtained forms a fundamental basis for the investigation of the effect of fuel volatility in connection with numerous problems dealing with engine performance and operation, the precise application to these problems is very limited due to the lack of adequate information on the departure from equilibrium vaporization in engine manifolds. Such information is urgently needed and when obtained should lead to a much better understanding of the relation between fuel volatility, operating conditions, and engine design factors. In a later paper there will be considered the application of the volatility relations to the problems of engine starting, acceleration, mixture distribution, and crankcase dilution on the basis of existing information.

Acknowledgment is made to the Cooperative Fuel Research Steering Committee of the automotive and petroleum industries for its active cooperation and financial support in connection with this investigation. Acknowledgment is also made to the late T. S. Sligh, who started the investigation and designed some of the apparatus used, and to D. C. Ritchie, who made a large number of the observations of experimental data herein reported.

WASHINGTON, May 14, 1934.